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**CLAIMS**

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[Claim(s)]

[Claim 1]In member holding which accommodates a lithium secondary battery which a plate-like case where a battery element which has an anode, a negative electrode, and an electrolyte consists of sheathing materials comes to store, Member holding for lithium secondary batteries characterized by vertical intensity being the intensity which can bear a pressure more than  $0.5 \text{ kg/cm}^2$  to a monotonous side of the above-mentioned case.

[Claim 2]The member holding for lithium secondary batteries according to claim 1 whose height of a seat part of member holding is 101 to 120% of the total thickness of a lithium secondary battery.

[Claim 3]A secondary battery pack which accommodates a lithium secondary battery which a plate-like case where a battery element which has an anode, a negative electrode, and an electrolyte becomes an inside of the member holding according to claim 1 or 2 from a sheathing material comes to store.

[Claim 4]The secondary battery pack according to claim 3 whose thickness of a sheathing material is 0.2 mm or less.

[Claim 5]The secondary battery pack according to claim 3 or 4 whose thickness of a lithium secondary battery is not less than 2 mm.

[Claim 6]A secondary battery pack of any one statement of claim 3 thru/or 5 whose nominal capacity of a cell is 100 or more mAh.

[Claim 7]A secondary battery pack of any one statement of claim 3 thru/or 6 in which a sheathing material consists of a laminate film in which a synthetic resin layer and a gas barrier layer were laminated.

[Claim 8]A secondary battery pack of any one statement of claim 3 thru/ or 7 in which a battery element has a non fluidity electrolyte between an anode and a negative electrode.

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[Translation done.]

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the rechargeable battery whose safety at the time of overcharge improved in detail about a rechargeable battery.

[0002]

[Description of the Prior Art]Danger, such as ignition according [ the developed lithium secondary battery of high energy density ] to the height of the energy density, therefore the misuse of a cell, failure of a use device, etc. and emitting smoke, is increasing in recent years. In the present cell design high-energy-density-ized more, reservation of the safety of a rechargeable battery is one of the indispensable technical problems from such a background.

[0003]Especially in safety reservation of a cell, the safety reservation to a surcharge is one of the important technical problems. It is because this has the relatively high danger of a cell being in an overcharging condition, and an internal short circuit etc. happening as a result, and leading to accidents, such as emitting smoke of a cell, and ignition, with the rise of battery temperature when charging a rechargeable battery and the electrical and electric equipment more than predetermined flows by a certain cause. For example, generally, if a lithium secondary battery will be in an overcharging condition, generating of gas will take place by disassembly of an electrolysis solution etc. first. When the generation of gas arises, when this state continues, it not only leads to the burst of a cell, a liquid spill, etc., but battery temperature may rise eventually and it may lead to accidents, such as emitting smoke and ignition.From such a viewpoint, various prevention methods for a surcharge have so far been proposed.

[0004]

[Problem(s) to be Solved by the Invention]It is known as a method with the common mechanical current cutoff method by the safety valve using the gas emitted by disassembly of the control method by the electronic circuit attached to the battery exterior, the electrolysis solution at the time of overcharge, etc. as the concrete method of a overcharge preventive measure, etc. However, in such a method, an electronic circuit and a safety valve are carried in a cell, and also [ required ] there was a problem that cell cost went up and restrictions of the design of a cell arose.

[0005]In recent years, a plate-like case is constituted using a lightweight sheathing material like the laminate film which provides a resin layer in both sides of a gas barrier layer, and the cell of the type which seals the battery element which has an anode and a negative electrode in this is developed. Since a lightweight film can be used for such a cell as a sheathing material, it has some advantageous points compared with the case which consists of conventional metal. That is, since the composition of a case is simpler compared with the case where the case which it not only can miniaturize, but consists a cell of a light weight and a metal can containing an electronic circuit and a safety valve more is used, becoming in cost and advantageous is also expected. On the other hand, in such a cell, the control method by the above-mentioned electronic circuit and the

mechanical current cutoff method by a safety valve have the problem of a cell case of being constitutionally especially difficult.

[0006]The method by the shutdown which, on the other hand, used fusion of the separator by the rise in heat of a cell as the concrete method of a overcharge preventive measure, By adding the overcharge inhibitor which has oxidation potential in electropositive potential from the anode potential at the time of a full charge to an electrolysis solution, when anode potential rises by an overcharging condition, how to trigger oxidation reaction of organic additives and inhibit the run away reaction in a cell at the time of overcharge is also known. However, since the shutdown method by the former separator has the rapid run away reaction at the time of overcharge, it is sometimes difficult to make it fully function as overcharge protection. In order to add the overcharge inhibitor which does not necessarily participate in the charge and discharge of a cell directly to an electrolysis solution in the latter method, have an adverse effect on battery capacity, or, Or gas is emitted as a result of oxidation reaction of the overcharge inhibitor at the time of overcharge, and we are anxious about the disclosure of poisonous gas, such as corrosion of a use device, and organic gas, by this generating gas, etc.

[0007]

[Means for Solving the Problem]As a result of repeating examination wholeheartedly that this invention persons should attain the above-mentioned purpose, generating of gas within a cell at the time of overcharge, It can control, if pressure more than specification which is in inter-electrode at the time of overcharge is added, And breakage and corrosive gas from a cell of a use device by bulging of a cell when generating of gas of a cell at the time of overcharge is controlled, Since a rise of battery temperature was also controlled, it found out that emitting smoke of a cell and danger to ignition could be reduced further, and it not only can prevent disclosure of toxic gas, but completed this invention.

[0008]That is, a gist of this invention consists below.

(1) In member holding which accommodates a lithium secondary battery which a plate-like case where a battery element which has an anode, a negative electrode, and an electrolyte consists of sheathing materials comes to store, Member holding for lithium secondary batteries characterized by vertical intensity being the intensity which can bear a pressure more than  $0.5 \text{ kg/cm}^2$  to a monotonous side of the above-mentioned case.

(2) Member holding for lithium secondary batteries of (1) whose height of a seat part of member holding is 101 to 120% of the total thickness of a lithium secondary battery.

A secondary battery pack which accommodates a lithium secondary battery which a plate-like case where a battery element which has an anode, a negative electrode, and an electrolyte becomes an inside of member holding of (3), (1), or (2) from a sheathing material comes to store.

(4) A secondary battery pack given in (3) whose thickness of a sheathing material is 0.2 mm or less.

(5) A secondary battery pack of (3) – (4) whose thickness of a lithium secondary battery is not less than 2 mm.

(6) A secondary battery pack of (3) – (5) whose nominal capacity of a cell is 100 or more mAh.

(7) A secondary battery pack of (3) – (6) in which a sheathing material consists of a laminate film in which a synthetic resin layer and a gas barrier layer were laminated.

(8) A secondary battery pack of (3) – (7) in which a battery element has a non fluidity electrolyte between an anode and a negative electrode.

[0009]

[Embodiment of the Invention]Hereafter, it explains per embodiment of this invention. The typical exploded perspective view of the member holding which requires drawing 18 for one embodiment of this invention, and drawing 19 are the A-A arrowed cross-section figures of drawing 18 showing signs that the battery element was stored by member holding. It may write for convenience among a figure a thickness direction [ the direction which shows the direction which shows the direction shown by x by a longitudinal direction and y by a cross direction and z ].

[0010]The member holding 181 consists of the barrel 181a and the two lids 181b and 181c. The barrel 181a is an open tube-like object which has an upper face part, an undersurface part, the front part, and a back part, and has the plate-like rectangular parallelepiped shape which spreads in a xy plane as a whole. The barrel 181a is the really molded member made of resin. The barrel 181a has a seat part (space part) which carries out an opening outside in the longitudinal direction in a figure. The lids 181b and 181c are the members made of resin of the flat plate shape which spreads in the yz direction, respectively, adhere with the barrel 181a in respect of the right and left of the barrel 181a, and isolate a seat part with the exterior. The barrel 181a and the lids 181b and 181c are screwed with the screw thread 182, respectively. The terminal area 182 connected with the anode of a battery element and the negative electrode is formed in the lid 181c.

[0011]A battery element is stored by the seat part. A battery element carries out two or more (in this case, 3) laminations of the unit battery element which laminates the anode 192a and the negative electrode 192b via the electrolyte layer (spacer) 193c in the above-mentioned laminating direction. A battery element has the flat plate shape which spreads in the xy direction as a whole. The vacuum lock of the battery element is carried out to the case which consists of the sheathing materials 191a and 191b of two sheets.

[0012]In this invention, more than  $0.5 \text{ kg/cm}^2$  makes preferably intensity of said member holding 181 of a vertical direction (in drawing 19, it is thickness direction z) more than  $0.6 \text{ kg/cm}^2$  to the monotonous side of the above-mentioned case which spreads in the xy direction. The yield of the gas by the decomposition reaction of the electrolysis solution which will press an electrode by a moderate pressure by member holding at the time of such strong \*\*\*\*\* for member holding and overcharge, and, as a result, serves as a trigger of the run away reaction of the cell at the time of overcharge can be decreased remarkably. Under anticipated-use conditions, since load inter-electrode [ this ] may lead to evils, such as a short circuit of a cell, it is preferred to design member holding so that pressure may be added to inter-electrode in an overcharging condition. That is, at the time of overcharge, especially the thickness of an electrode increases notably from near the charge depth which the dedope of the lithium ion from an anode ends. Therefore, as for member holding, when this phenomenon is used, it is considered as the thickness of member holding which does not press an electrode at the time of anticipated use and an electrode blisters at the time of overcharge, it is preferred to consider it as the thickness of member holding which sticks to a cell, and stops bulging, namely, presses a cell. It is preferred to specifically make the height ( $L_2$  shows drawing 19) of the seat part of member holding into 101 to 120% of the total thickness ( $L_1$  shows drawing 19) of a lithium secondary battery in consideration of there being bulging of few cells with charging a cell under an anticipated-use condition.

[0013]Since what has the above-mentioned, too much large intensity of member holding is actually difficult to get, below  $50 \text{ kg/cm}^2$  usually makes [ below  $100 \text{ kg/cm}^2$  ] it desirable. The above-mentioned intensity of member holding is controllable by material, its attachment intensity, etc. of member holding. In the above-mentioned example, although the member holding 181 used the thing made of resin, the material in particular is not limited, for example, it can use various kinds of materials, such as a hybrid of metal, and resin and metal. In the above-mentioned example, although the barrel 181a and the lids 181b and 181b were attached with the screw thread, it is not limited in particular, for example, it can stop with adhesives or adhesive tape, or can fix with a nail.

[0014]In the above-mentioned example, although what consists of the barrel 181a and the lids 181b and 181b was used for the member holding 181, In addition, the member holding which consists of the barrel 181a and the lid 181b of the owner bottom which carries out an opening only to one side as shown, for example in drawing 20, The member holding which consists of the barrel 181a and the lid 181b of the owner bottom which carries out an opening to the upper part (thickness direction) as shown in drawing 21, and the member holding which supports the plate shaped member 184a of an up-and-down couple as shown in drawing 22 with the leg object 185 of plurality (in this case, 4) can

be used. Also in these cases, the barrel 181a and the lid 181b are \*\*\*\*ed, and are attached with a nail, adhesives, adhesive tape, etc.

[0015]The secondary battery pack in which the member holding 181 comes to store a battery element is usually used, being connected to other cell use devices. As such a cell use device, a cellular phone, a personal digital assistant, portable audio equipment, A cordless phone cordless handset, a cell book player, a pager, a handy terminal, Portable fax, a portable copy, a portable printer, a headphone stereo, A video movie, a liquid crystal television, a handy cleaner, portable CD, Various kinds of apparatus, such as medical equipment, such as an electrical machinery shaver, an electronic translating machine, a car telephone, a transceiver, a power tool, an electronic notebook, a calculator, memory card, a tape recorder, radio, a backup power supply, a camera, a pacemaker, and hearing aid, can be mentioned. Various kinds of functions (a circuit, a driver, etc.) are attached in a battery pack, and the battery pack itself can also be made into a cell use device.

[0016]Next, the lithium secondary battery stored by member holding is explained. When the lithium secondary battery used by this invention has too thin the thickness of the whole lithium secondary battery which the plate-like case where the battery element which has an anode and a negative electrode consists of sheathing materials comes to store, since there are few yields of the gas at the time of overcharge relatively, Especially especially in the case of not less than 2 mm, the effect of this invention is remarkable 1 mm or more. Since it miniaturizes and is hard to carry out the weight saving of the cell, 4 mm or less is of 5 mm or less usually on the other hand too much thick still more preferably 4.5 mm or less preferably.

[0017]Since the cell with small capacity of a cell has relatively few yields of the gas at the time of overcharge, 100 or more mAh of lithium secondary batteries in 200 or more mAh are usually preferably used for it as nominal capacity. A battery element has an anode and a negative electrode. There is no restriction in particular in the shape of a battery element, and various kinds of shape which can be stored in a plate-like case can be adopted. For example, the monotonous lamination type shape which carries out two or more (in this case, 3) laminations of the plate-like unit battery element which laminates the anode 192a as shown in drawing 19, and the negative electrode 192b via the electrolyte layer (spacer) 193c as a battery element in the above-mentioned laminating direction is employable. The winding mold configuration which winds the band-like layered product which laminated the anode and the negative electrode via the electrolyte layer is also employable.

[0018]The lithium secondary battery by which sealing storage was carried out with the sheathing material of film state in the battery element which laminates hereafter two or more plate-like unit battery elements which have an anode, a negative electrode, and a non fluidity electrolyte layer to a thickness direction is made into an example, and is explained to details per embodiment of a lithium secondary battery. The exploded perspective view of the cell which requires drawing 1 for an embodiment, and drawing 2 The sectional view of the important section of this cell, It is a typical sectional view showing signs that the perspective view of a cell blisters, as for the perspective view with rough drawing 3, drawing 4, and drawing 5 of a battery element, the sectional view ((a) is a whole sectional view and (b) is an expanded sectional view of B portion of (a)) of a case blisters, as for drawing 6, and a cell blisters, as for drawing 7. A cell given in the expedient top of explanation and drawing 1 is carried out for upside down, and it is shown in drawing 4 and drawing 5.

[0019]After this cell accommodates the battery element 1 in the crevice of the sheathing material 3, it pours in the insulating materials 5, such as an epoxy resin and an acrylic resin, near the terminal area (tabs 4a and 4b) of the battery element 1, puts the sheathing material 2 on the sheathing material 3 after that, and joins the edge parts 2a and 3a of the sheathing materials 2 and 3 by a vacuum lock. The sheathing material 2 is plate-like as drawing 1. The sheathing material 3 is a thing of the shape of a shallow non-lid box with the seat part 3b which consists of a crevice of rectangular case shape, and the edge part 3a jutted out of four peripheries of this seat part 3b over flange shape at the method of outside.

[0020]The battery element 1 laminates two or more unit battery elements to a thickness direction

as drawing 3. From this unit battery element, the tab 4a or 4b is pulled out. Each tab 4a from an anode is bundled (that is, pile up mutually and be put together), the positive electrode lead 21 is joined, and the positive pole terminal part is formed. Tab 4b from a negative electrode is bundled, the negative electrode lead 21 is joined, and the negative pole terminal part is formed.

[0021]After the battery element 1 is accommodated in the seat part 3b of the sheathing material 3, the insulating material 5 is poured in the tab 4a and near the 4b and the battery element side a positive pole terminal part and near the negative pole terminal part is covered with an insulating material, the sheathing material 2 is put. One pair of leads 21 which extended from the battery element 1 are pulled out outside through the edge part 2a of one side part of the sheathing materials 2 and 3, and the mating face of 3a, respectively. Then, the edge part 2a of four peripheries of the sheathing materials 2 and 3 and 3a are airtightly joined by techniques, such as thermo compression bonding and ultrasonic welding, under decompression (preferably vacuum) atmosphere, and the battery element 1 is enclosed in the sheathing material 2 and 3. Then, curing treatment is presented with the insulating material 5 by heating etc., and the insulating material 5 adheres thoroughly near the terminal area. Since the sheathing material is closed before adhering thoroughly, the shape of a cell hardly changes at the time of adherence.

[0022]The case which consists of the sheathing materials 2 and 3 is constituted by joining the edge part 2a and 3a. This case is provided with the following as shown in drawing 4.

The entire-covering part 4B of the approximately rectangular parallelepiped shape which wraps the battery element 1 entirely by side wall part 4B<sub>1</sub>, raised bottom part 4B<sub>2</sub>, and a lower base part (not shown).

The edge part 2a of said sheathing material, the joining piece parts 4A, 4F, and 4G to which it comes to join 3a.

[0023]In the state given in drawing 4, the above-mentioned joining piece parts 4A, 4F, and 4G are jugged over the method of outside out of side wall part 4B<sub>1</sub> of the entire-covering part 4B which has wrapped the battery element 1 entirely. Then, as shown in drawing 5, among these joining piece parts, the joining piece parts 4A and 4G are bent so that side wall part 4B<sub>1</sub> of the entire-covering part 4B may be met, and the thing (it fixes) stick to side wall part 4B<sub>1</sub> of the entire-covering part 4B with adhesives is made. That is, for example, as shown in drawing 6, the joining piece part 4A is bent along with side wall part 4B<sub>1</sub> of the entire-covering part 4B, and these are mutually pasted up with the adhesives 51. As the adhesives 51, various kinds of things, such as epoxy adhesive, acrylic adhesives, urethane system adhesives, hot melt system adhesives, and synthetic rubber system adhesives, can be used. Of course, two or more adhesives can also be used together. In order to control the fixing strength of a joining piece part and a side wall part, in selection of adhesives, it is necessary to take into consideration the construction material of the surface of a joining piece part and a side wall part, the environment at the time of fixing work (humidity, temperature, etc.), etc. but, and. Preferably, cure time is short and uses the hot melt system adhesives easily hardened under the low environment of the dew point used in the case of manufacture of a nonaqueous cell.

[0024]Thus, as for these joining piece parts, although it can adhere to side wall part 4B<sub>1</sub> in at least a part of joining piece part (joining piece parts 4A and 4G), adhering with predetermined fixing strength is preferred in this case. That is, when the following fixing strength examination is done, said joining piece part adheres 20 degrees or less still more preferably 30 degrees or less by the intensity of the grade which can maintain the angle of 10 degrees or less most preferably preferably 45 degrees or less to said entire-covering part.

Charging the cell which has fixing strength testing cell voltage in 3V with the current of 1.8C is continued for 200 minutes in the range which set upper limit voltage to 10V. However, 1C is a current value for discharging the capacity charged and obtained in 1 hour until a current value is set

to 0 from the cell voltage 2.7V with 4.2V constant voltage. The angle of the flat surface where the angle of the joining piece part and entire-covering part in the portion which adhered includes the adhesion side of a joining piece part, and a flat surface including the adhesion side of an entire-covering part to make (in drawing 6, it is an angle of S1 and S2 to make.) In this case, it is a thing on account of [ zero ] parallel.

[0025]Generally, a cell tends to blister in an overcharging condition. Namely, as shown in drawing 7 at the time of overcharge, a cell tends to blister in the direction P. In this invention, a battery element is accommodated in the member holding of said predetermined intensity so that bulging to this direction P may be prevented. As a result, a safer cell can be provided in an overcharging condition. This will prevent effectively bulging generated the first stage at the time of overcharge, and is presumed to have inhibited the run away reaction of the cell after it.

[0026]In the above example, although the joining piece parts 4A and 4G have adhered to side wall part 4B<sub>1</sub> with adhesives, they are not limited to the method of adherence using adhesives. For example, a joining piece part can be made to adhere to an entire-covering part using adhesive tape.

[0027]In the above-mentioned example, although the joining piece parts 4A and 4G are bent only once along with side wall part 4B<sub>1</sub>, For example, the joining piece part 4A is bent further once again on the way, and it may be made to make the tip of the joining piece part 4A intervene between the joining piece part 4A and side wall part 4B<sub>1</sub>, as shown in drawing 8. Thus, by carrying out two or more diffraction music of the joining piece part, air etc. can be prevented from invading from the side of a joining piece part, or the mechanical strength in a side wall part can be raised further.

[0028]At drawing 1, although the sheathing materials 2 and 3 serve as a different body, by this invention, the sheathing materials 2 and 3 may serve as series one like drawing 9. In drawing 9, one side of the sheathing material 3 and one side of the sheathing material 2 stand in a row, and the sheathing material 2 serves as the shape of a lid which stands in a row turnable to the sheathing material 3. The crevice of the seat part 3b is formed, and except that the joining piece part is not formed in this one side, it becomes a thing of the same composition as a joining piece part from one side with which these sheathing materials 2 and 3 are connected. Also in the case of this drawing 9, the joining piece parts 4A and 4G adhere to side wall part 4B<sub>1</sub> with adhesives.

[0029]Although the sheathing material 3 with the seat part 3b and the plate-like sheathing material 2 are shown by drawing 1 and 9, In this invention, the battery element 1 may be entirely wrapped like drawing 10 with the sheathing materials 6 and 7 with the shallow box-like seat parts 6b and 7b and the edge parts 6a and 7a jutted out of four peripheries of these seat parts 6b and 7b, respectively. In drawing 10, although the sheathing materials 6 and 7 serve as a series object, these may serve as a different body like said drawing 1.

[0030]In drawing 1 and 9 or 10 composition, since the seat part of the battery element is formed beforehand, a battery element can be accommodated more in a compact, and the accommodation itself is easy. In the above-mentioned explanation, after accommodating a battery element in a seat part, the insulating material is poured in near the terminal area, but an insulating material adheres and flows between the mating face of an edge part, a battery element, and a sheathing material in this case, and junction of an edge part may be checked or it may not become the cell shape as a design. Then, after supplying an insulating material near the terminal area of a battery element, the above-mentioned problem is avoidable by accommodating a battery element in a seat part. Since an insulating material cannot be supplied to the abbreviated upper half of a battery element even if especially in the case of drawing 10 it supplies an insulating material after accommodating a battery element, this manufacturing method is preferred. On the other hand, in this method, since the handling in the state where the insulating material was supplied needs to carry the battery element which is not easy and needs to arrange to a sheathing material, cautions are required for the handling at the time of manufacture. It can be said that the former method is preferred in this point.

[0031]In this invention, turn up the sheet shaped flat sheathing material 8 of one sheet in the shape



of 2 Thu chip boxes along with the central neighborhood 8a like drawing 11, and two pieces with 8B are formed the 2nd piece with 8A the 1st piece, These 1st pieces of the battery element [ the 2nd piece of ] 1 is made to intervene between 8B with 8A, like drawing 12, piece [ 1st ] edge part 8b [ piece / 2nd ] of 8B may be joined to 8A, and the battery element 1 may be enclosed. Also in this case, the joining piece parts 4A and 4G adhere to side wall part 4B<sub>1</sub> of the entire-covering part which wraps the battery element 1 entirely with adhesives. Since a joining piece part is made to meet an entire-covering part, it bends and it is fixing with adhesives or adhesive tape further even if it is in the cell constituted in this way, the blister of the battery element in the early stages of a surcharge can be effectively prevented also in this case, and the intensity of the side of a cell and rigidity are high. Of course, the bent joining piece part is prevented also from deserting an entire-covering part. Since the intensity of the side of a cell and rigidity are high, peeling is prevented from arising by the active material even when shocked by the side.

[0032]Although the joining piece parts 4A and 4G have adhered to side wall part 4B<sub>1</sub> of the entire-covering part 4B, they can also make it adhere to portions other than a side wall part in the above example. For example, as shown in drawing 17, where the lead 21 is pulled out, wrap entirely, so that the circumference of a battery element may be wound for the sheathing material 2 of one sheet, and the periphery of a sheathing material is joined, When the joining piece part 4F provided in the portion which pulled out the lead, the joining piece part 4G provided in that opposing side, and the joining piece part 4H provided over the upper surface 4I of an entire-covering part are made to form, this joining piece part 4H and the entire-covering part upper surface 4I can also be adhered with adhesives or adhesive tape.

[0033]In the above example, it fills up with the insulating material 5 near the terminal area (tabs 4a and 4b). As a result, the blister of the battery element in the early stages of a surcharge can be prevented effectively, and a short circuit is prevented further more effectively. As the insulating material 5, a synthetic resin is preferred, and although an epoxy resin, an acrylic resin, silicone resin, etc. are illustrated, since cure time is short, an epoxy resin or an acrylic resin is especially preferred. Since a possibility of having an adverse effect on battery capacity is low, especially an acrylic resin is the most preferred. An insulating material is supplied near the terminal area in the state that it does not harden and of being liquid, and adheres near the terminal area thoroughly by hardening. In drawing 1, as for the insulating material 5, although supplied separately, respectively, in order [ of a positive pole terminal part and a negative pole terminal part ] to improve the safety at the time of overcharge more, it is more preferred to cover the whole side of a battery element ranging from the positive pole terminal part to a negative pole terminal part. In covering of the battery element side near [ this ] the terminal area, it is preferred to form a larger spacer than these between an anode and a negative electrode, and to adhere mutually in the flash parts of this spacer especially.

[0034]That is, if it is in a battery element, as shown, for example in drawing 16, the spacer 13 made the anode 11 and the negative electrode 13 overflow a little, formed the flash part 13a, and has prevented the short circuit of the anode 11 and the negative electrode 13. Since a battery element is restrained by the laminating direction by adhering by an insulating material in these flash part 13a, even if it is at the overcharge time, bulging of a battery element is prevented, and the thermal run-away of a cell is prevented. Of course, an insulating material can be continued and supplied to the whole side of a battery element, and is preferred.

[0035]As for the sheathing material which stores a battery element, what has shape changeability is preferred. As a result, when a sheathing material is closed under a vacua, it can give the function which strengthens the inter-electrode lamination of a battery element, and, as a result, it is not only easy to create the cell of various shape, but can raise battery characteristics, such as a cycle characteristic. Since the volume energy density and weight energy density of a cell become larger as the thickness of a sheathing material is thin, since the intensity itself is relatively low, it is not



only desirable, but the effect of this invention becomes remarkable especially. The thickness of a sheathing material is usually 0.15 mm or less preferably 0.2 mm or less. However, since insufficient strength becomes remarkable and becomes easy to penetrate moisture etc., 0.02 mm or more is usually too much thin preferably 0.01 mm or more.

[0036]As a material of a sheathing material, metal, such as aluminum, iron which carried out the nickel plate, and copper, a synthetic resin, etc. can be used. Preferably, they are the laminate film in which the gas barrier layer and the resin layer were provided, and the laminate film in which the resin layer was especially provided in both sides of the gas barrier layer. Such a laminate film has high gas barrier property, and it has high shape changeability and thinness. As a result, thin-film-izing and the weight saving of a sheathing material can become possible, and the capacity as the whole cell can be raised.

[0037]As a material of the gas barrier layer used for a laminate film, metallic oxides, such as alloys, such as metal and stainless steel, such as aluminum, iron, copper, nickel, titanium, molybdenum, and gold, and Hastelloy, silicon oxide, and an aluminum oxide, can be used. Preferably, it is lightweight and is aluminum which is excellent in processability. As resin used for a resin layer, various kinds of synthetic resins, such as thermoplastics, thermoplastic elastomer, thermosetting resin, and a plastic alloy, can be used. That with which fillers, such as a filler, are mixed is also included in these resin.

[0038]As composition of a concrete laminate film, as shown in drawing 13 (A), that by which the gas barrier layer 40 and the resin layer 41 were laminated can be used. A desirable laminate film, As shown in drawing 13 (B), form the synthetic resin layer 41 for functioning as an outside protective layer in the lateral surface of the gas barrier layer 40, and. It is considered as 3 layered structure which laminated the synthetic resin layer 42 which functions as an inside protective layer for preventing contact with the corrosion and the gas barrier layer by an electrolyte, and a battery element to a medial surface, or protecting a gas barrier layer.

[0039]In this case, the resin used for an outside protective layer has the desirable resin which was preferably excellent in chemical resistance, such as polyethylene, polypropylene, denaturation polyolefine, an ionomer, amorphous polyolefin, polyethylene terephthalate, and polyamide, or a mechanical strength. As an inside protective layer, a chemical-resistant synthetic resin is used, for example, polyethylene, polypropylene, denaturation polyolefine, an ionomer, an ethylene-vinylacetate copolymer, etc. can be used.

[0040]The laminate film can also form the adhesive layer 43, respectively between the gas barrier layer 40, the synthetic resin layer 41 for protective layer formation, and the synthetic resin layer 42 for corrosion-resistant layer formation, as shown in drawing 14, and it is preferred. In order to paste up sheathing materials, the glue line which consists of resin which can be innermost welded [ of composite ], such as polyethylene and polypropylene, can also be provided further again. A case is formed using these metal, a synthetic resin, or composite. Shaping of a case may weld and form the circumference of a film like body, and may carry out draw forming of the sheet like body by vacuum forming, pressure forming, press forming, etc. It can also fabricate by carrying out injection molding of the synthetic resin. When based on injection molding, usually a gas barrier layer is formed of sputtering etc.

[0041]For providing beforehand, spinning etc. can perform the seat part which becomes a sheathing material from a crevice. As for a sheathing material, it is preferred that processing uses the thing of film state at an easy point. The battery element which has an anode, a negative electrode, and an electrolyte is stored in a case. As mentioned above, the battery element can wind the layered product (unit battery element) which consists of an anode, a negative electrode, and an electrolyte layer, can make it winding shape, and can also store this in a case, and can also store the above-mentioned layered product (unit battery element) in a case with flat plate shape as it is. Like the statement to said drawing 2 and 3, two or more unit battery elements can be laminated to a thickness direction, and it can also be considered as a battery element. The suitable composition of a unit battery element is explained below.

[0042] Drawing 15 shows an example with a preferred unit battery element which consists of this lithium secondary battery. This unit battery element laminates the negative electrode which consists of the anode, the spacer (electrolyte layer) 24, the negative electrode active material layer 25, and the negative pole collector 26 which consist of the positive pole collector 22 and the positive active material layer 23. In order to control the deposit of a lithium dendrite, a negative electrode is made larger than an anode. In order to prevent a short circuit, the spacer 24 is made larger than an anode and a negative electrode. By making a spacer larger than positive and negative poles, it can adhere in both the flash parts of the spacer of a unit battery element as mentioned above.

[0043] Although two or more these unit battery elements are laminated and it is considered as a battery element, on the occasion of this lamination, the unit battery element of the order posture (drawing 15) which made the anode the upper part and made the negative electrode the bottom, and this laminate by turns the unit battery element of the reverse posture (graphic display abbreviation) which made the anode the bottom conversely and made the negative electrode the upper part. That is, the unit battery element which adjoins a laminating direction is laminated so that like poles (namely, anodes and negative electrodes) may meet.

[0044] The positive electrode tab 4a is installed from the positive pole collector 22 of this unit battery element, and the negative electrode tab 4b is installed from the negative pole collector 26. In drawing 15, although it has indicated that the \*\*\*\*\* positive active material layer and the negative electrode active material layer are formed in one side of a positive pole collector, and one side of a negative pole collector, of course, an active material layer can be formed in both sides of a charge collector. In this case, the active material layer by which the same charge collector of each other was formed in the opposite field can be made into the component of a unit battery element which differs mutually.

[0045] The plane shape of an electrode is arbitrary and can be made into a quadrangle, circular, a polygon, etc. The tabs 4a and 4b for lead combination are usually formed successively by the charge collectors 22 and 26 as drawing 15. When an electrode is a quadrangle, as usually shown in drawing 3, the tab 4a which projects from a positive pole collector near the side of one side of an electrode is formed, and the tab 4b of a negative pole collector is formed near the other side.

[0046] It is effective to laminate two or more unit battery elements, when attaining high capacity-ization of a cell, but in this case, each of the tab 4a from each unit battery element and the tab 4b is usually combined with a thickness direction, and the terminal area of an anode and a negative electrode is formed. As a result, it becomes possible to obtain the mass battery element 1. As shown in drawing 2, the lead 21 which consists of metal of a thin film integrated circuit is combined with the tabs 4a and 4b. As a result, the anode and negative electrode of the lead 21 and a battery element are combined electrically. Resistance welding of spot welding etc., ultrasonic welding, or laser welding can perform combination of tab 4a and 4b, and combination with the tabs 4a and 4b and the lead 21.

[0047] at least one lead 21 of the above-mentioned positive electrode lead and a negative electrode lead -- it is preferably preferred as both leads to use annealing metal. As a result, it can be considered not only as intensity but as the cell which broke, bent and was excellent in endurance. Generally as a kind of metal used for a lead, aluminum, copper and nickel, SUS, etc. can be used. A material desirable as a lead of an anode is aluminum. Construction material desirable as a lead of a negative electrode is copper.

[0048] 1 micrometers or more of thickness [ not less than 10 micrometers of / not less than 20 micrometers of ] of the lead 21 are usually not less than 40 micrometers most preferably still more preferably. When too thin, it is in the tendency for mechanical strengths of a lead, such as tensile strength, to become insufficient. 500 micrometers or less of thickness of a lead are of 1000 micrometers or less usually 100 micrometers or less still more preferably preferably. It is in the tendency to be in the tendency to bend and for endurance to get worse when too thick, and for closure of the battery element in a case to become difficult. The advantage by using the annealing

metal later mentioned to a lead is so remarkable that the thickness of a lead is thick.

[0049]The exposure length to the exterior of a lead is usually 1 mm or more about 50 mm or less. As mentioned above, although a battery element may be a wound type cell which winds the layered product (unit battery element) which laminated the anode and the negative electrode via the electrolyte layer, it is preferred to make a spacer intervene between an anode and a negative electrode also in this case, and to make this larger than positive and negative poles.

[0050]Hereafter, the material used for a lithium secondary battery is explained. A battery element usually has an anode, a negative electrode, and an electrolyte layer that exists among them. An anode and a negative electrode usually contain a charge collector and the active material layer provided on it. As a positive pole collector, although various kinds of metal, such as aluminum, nickel, and SUS, can be used, it is aluminum preferably. The thickness of a charge collector is not less than 5 micrometers still more preferably, and is of 1 micrometers or more usually 20 micrometers or less still more preferably 25 micrometers or less preferably of 30 micrometers or less usually not less than 3 micrometers. As thin, it is more desirable from a viewpoint of volume energy density and weight energy density, but the handling of too much thin one becomes difficult easily in respect of intensity etc. Charge collectors may be tabular [ like the usual metallic foil ], and mesh state like a punching metal. The surface roughening process of the surface of a charge collector can be carried out if needed.

[0051]As an active material which uses for an anode and can do things, it is considered as the compound which can occlusion emit a lithium ion, and an inorganic compound or an organic compound can also be used. As an inorganic compound, the oxide of transition metals, such as Fe, Co, nickel, and Mn, the multiple oxide of lithium and a transition metal, transition metal sulfide, etc. are mentioned. As a transition metal oxide, specifically  $\text{MnO}_2$  and  $\text{V}_2\text{O}_5$ ,  $\text{V}_6\text{O}_{13}$ ,  $\text{TiO}_2$  etc. can be illustrated, nickel acid lithium, cobalt acid lithium, manganic acid lithium, etc. can be illustrated as a multiple oxide of lithium and a transition metal, and  $\text{TiS}_2$ ,  $\text{FeS}$ , etc. can be illustrated as transition metal sulfide. As an organic compound, conductive polymers, such as poly aniline, etc. are mentioned, for example. The arbitrary methods of carrying out quantity mixing and using as positive active material are also suitably used in these arbitrary inorganic compounds and an organic compound. It is a multiple oxide which contains preferably the multiple oxide of lithium and a transition metal, at least one sort of transition metal oxides chosen from the group which consists of manganese, nickel, and cobalt especially, and lithium. Especially, the multiple oxide containing cobalt and lithium and the multiple oxide containing nickel and lithium are preferred. The particle diameter of positive active material is a point of battery characteristics, such as a rate characteristic and a cycle characteristic, and is usually 1–10 micrometers preferably 1–30 micrometers.

[0052]As a negative pole collector, although various kinds of metal, such as copper, nickel, and SUS, can be used, it is copper preferably. The thickness of a charge collector is not less than 5 micrometers still more preferably, and is of 1 micrometers or more usually 20 micrometers or less still more preferably 25 micrometers or less preferably of 30 micrometers or less usually not less than 3 micrometers. As thin, it is more desirable from a viewpoint of volume energy density and weight energy density, but the handling of too much thin one becomes difficult easily in respect of intensity etc. Charge collectors may be tabular [ like the usual metallic foil ], and mesh state like a punching metal. The surface roughening process of the surface of a charge collector can be carried out if needed.

[0053]As an active material which can be used for a negative electrode, various kinds of compounds which can occlusion emit lithium outside a lithium metal can be used. Specifically, carbon materials, such as lithium alloy; graphite, such as a lithium metal; lithium aluminum alloy, a lithium bismuth cadmium alloy, and a lithium \*\*\*\*- cadmium alloy, and corks, etc. can be mentioned. Oxides and lead sulfate, such as silicon, tin, zinc, manganese, iron, and nickel, can also be used. Since it is in the

tendency for the safety at the time of overcharge to fall that it is especially easy to generate a dendrite in the case of charge when a lithium metal and a lithium alloy are used, carbon materials, such as graphite and corks, are preferred. The particle diameter of negative electrode active material is a point of battery characteristics, such as initial efficiency, a rate characteristic, and a cycle characteristic, and is usually 15–30 micrometers preferably 1–50 micrometers.

[0054]The active material layer of an anode and a negative electrode usually contains a binder outside the above-mentioned active material. As a binder to be used, it needs to be stable to an electrolysis solution etc., and weatherability, chemical resistance, heat resistance, fire retardancy, etc. are desired. As a binder, silicate, an inorganic compound like glass, and various kinds of resin that mainly consists of polymers can be used. As resin, for example, alkane system polymer; polybutadienes, such as polyethylene, polypropylene, and Poly 1,1-dimethylethylene, Unsaturation system polymer, such as polyisoprene; Polystyrene, polymethylstyrene, Polymer which has rings, such as polyvinyl pyridine and Poly N-vinyl pyrrolidone; Poly methyl methacrylate, Ethyl polymethacrylate, butyl polymethacrylate, poly(methyl acrylate), Acrylic derivative system polymer, such as ethyl polyacrylate, polyacrylic acid, polymethacrylic acid, and polyacrylamide; Polyvinyl fluoride, Fluororesin, such as polyvinylidene fluoride and polytetrafluoroethylene; Polyacrylonitrile, CN basis content polymer, such as a polyvinylidenecyanide; conductive polymers, such as containing halogen polymer; poly aniline, such as polyvinyl alcohol system polymer; polyvinyl chloride, such as polyvinyl acetate and polyvinyl alcohol, and a polyvinylidene chloride, etc. can be used. It can be used even if it is mixtures, such as the above-mentioned polymer, a conversion object, a derivative, a random copolymer, an alternating copolymer, a graft copolymer, a block copolymer, etc. The molecular weight of these resin is 100000–1 million preferably [ it is desirable and ] to 10000–3 million and a pan. If too low, the intensity of an active material layer will fall, and when too high, it is in the tendency for viscosity to become high and for formation of an electrode to become difficult.

[0055]As loadings of the binder to 100 copies of active materials, 0.1 to 30 copies are one to 20 copies still more preferably preferably. When there is too little quantity of a binder, the intensity of an electrode may fall, and when too large, it is in the tendency for ionic conductivity to fall. In an active material layer, a granular material, a filler, etc. which reveal various kinds of functions, such as an electrical conducting material and a reinforcing member, if needed may be contained. If it mixes to the above-mentioned active material in proper quantity and conductivity can be given to it as an electrical conducting material, there will be no restriction in particular, but the end of carbon powder, such as acetylene black, carbon black, and black lead, the fiber of various kinds of metal, foil, etc. are usually mentioned. The DBP oil absorption of a conductive substance is preferred in not less than 120cc/100 g, and preferred in the end of carbon powder from the reason for holding an electrolysis solution in not less than 150cc/100 g especially. As a reinforcing member, various kinds of inorganic and organic globular shapes, a fibrous filler, etc. can be used.

[0056]An electrode can be manufactured by applying and drying the paint containing the material which constitutes an active material layer on a charge collector. Consolidation processing can also be presented with an active material layer after that. The volume fraction of the binder in an active material layer is controllable by controlling the presentation of a paint, a drying condition, a consolidation condition, etc. Since the adhesive property between an active material layer and a charge collector is raised if needed, an undercoat primer layer can be provided among these.

[0057]When using an undercoat primer layer, the resin which added conductive particles, such as carbon black, graphite, and metal powder, as the presentation, and conductive organic conjugated system resin can be illustrated. It is good to use preferably the carbon black which may function on a conductive particle also as an active material, and graphite. When poly aniline, polypyrrole, poly acene, a disulfide system compound, a polysulfide system compound, etc. which may function as active materials also as resin are used, it is desirable in order not to decrease capacity. As for the rate of resin over a conductive particle, in the presentation which uses as the main ingredients the resin which added the conductive particle, it is preferred to consider it as 1 to 300 % of the weight.

When too low, film strength may fall and the exfoliation on a process, etc. may arise at the time of cell use. When too high, it is in the tendency for conductivity to fall and for a battery characteristic to fall. It is preferred to consider it as 5 to 100% of the weight of the range preferably especially.

0.05–10 micrometers of thickness of an undercoat primer layer are usually 0.1–1 micrometer preferably. If too thin, spreading will become difficult and it will become difficult to secure homogeneity. When too thick, the volume capacity of a cell may be spoiled more than needed.

[0058]An electrolyte exists as a constituent of the electrolyte layer between an anode and a negative electrode. An electrolyte usually exists also in the active material of an electrode as an ion migration phase. As an electrolyte, the thing of various kinds of descriptions, such as an electrolysis solution, a solid polymer electrolyte, a gel electrolyte, and an inorganic solid electrolyte, can be used, for example. Generally, if non fluidity electrolytes, such as a solid polymer electrolyte, a gel electrolyte, and an inorganic solid electrolyte, are used, it will become possible to prevent the leakage to electrolytic case outside more effectively. Since it is in the tendency for an electrolyte to leak to case outside easily when what has shape changeability is especially used as a case in this invention, especially the effect that uses a non fluidity electrolyte is remarkable.

[0059]On the other hand, the electrolysis solution which dissolves lithium salt in a nonaqueous solvent has high mobility, and is in the tendency to excel in ion conductivity compared with a non fluidity electrolyte generally. Therefore, it is preferred to use the electrolyte containing an electrolysis solution at the point which raises ion conductivity. The electrolysis solution used as an electrolyte dissolves lithium salt which is usually a supporting electrolyte in a nonaqueous solvent. As a nonaqueous solvent, the solvent of high permittivity is used comparatively suitably. Specifically Cyclic carbonate, such as ethylene carbonate and propylene carbonate. Non-cyclic carbonate, such as dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate. Nitril, such as sulfur compounds, such as lactone, such as ether, such as a tetrahydrofuran, 2-methyltetrahydrofuran, dimethoxyethane, and diphenyl ether, and gamma-butyrolactone, and sulfolane, and acetonitrile, can be mentioned. They are cyclic carbonate and/or lactone preferably on battery characteristics, such as a cycle characteristic, a rate characteristic, and safety.

[0060]In this invention, the boiling point in ordinary pressure uses a not less than 150 \*\* nonaqueous solvent (it may be called the following "high boiling point solvent") preferably as a solvent of an electrolysis solution. Here, in addition, "the boiling point is not less than X \*\*" means that steam pressure does not exceed 1atm even if it heats from a room temperature to X \*\* under pressure 1atm. That is, when it heats from a room temperature to 150 \*\* under pressure 1atm, it is preferred that steam pressure always uses the nonaqueous solvent which is 1 or less atm. As a result, the higher cycle characteristic has been acquired enough and the safety of a cell can be raised. For example, when the low-boiling point solvent which consists of solvents, such as dimethyl carbonate, diethyl carbonate, and dimethoxyethane, is used, It is generated by air bubbles between an active material and a solvent by evaporation of a solvent, the impregnation states of an electrolysis solution fall, and the heterogeneity of an interface arises, and it is in the tendency for a cycle characteristic to fall easily. Even if it stores a battery element in a shape changeability case by using a high boiling point solvent, the shape change (modification) of the cell in the bottom of an elevated temperature, etc., volatilization of an electrolysis solution, disclosure, etc. can also be controlled. As such a high boiling point solvent, propylene carbonate, ethylene carbonate, butylene carbonate, gamma-butyrolactone, etc. can be mentioned.

[0061]As for a nonaqueous solvent, it is preferred that viscosity is 1 or more mPa·s. As lithium salt which is a supporting electrolyte used for an electrolyte,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiI}$ ,  $\text{LiBr}$ ,  $\text{LiCl}$ ,  $\text{LiAlCl}_2$ ,  $\text{LiHF}_2$ ,  $\text{LiSCN}$ ,  $\text{LiSO}_3\text{CF}_2$ , etc. can be mentioned. Especially among these,  $\text{LiPF}_6$  and  $\text{LiClO}_4$  are preferred. The content in the electrolysis solution of these supporting electrolytes is usually 0.5 – 2.5 mol/l.

[0062]A gel electrolyte can consist of an above-mentioned electrolysis solution and polymer for gel

formation. A gel electrolyte usually holds the above-mentioned electrolysis solution by polymer. a gel electrolyte gives ion conductivity comparable as an electrolysis solution -- since things can be carried out and immobilizing of the electrolyte is carried out, in this invention, it is an especially desirable electrolyte. Although the concentration to the electrolysis solution of polymer in a gel electrolyte is based also on the molecular weight of the polymer to be used, it is usually 0.1 to 30 % of the weight. If concentration is too low, it will become difficult to form gel, and the holdout of an electrolysis solution may fall, and the problem of a flow and liquid leakage may arise. If concentration is too high, while viscosity will become high too much and will produce process top difficulty, it is in the tendency for the rate of an electrolysis solution to fall, for ionic conductivity to fall, and for battery characteristics, such as a rate characteristic, to fall. As polymer to hold, an electrolyte Poly (meta) acrylate system polymers, Various kinds of polymer which has a function which can gel an electrolysis solution, such as alkylene oxide system polymers which have an alkylene oxide unit, polyvinylidene fluoride, fluorine system polymers like a fluoridation vinylidene-hexafluoropropylene copolymer, can be mentioned.

[0063]Material and processes as occasion demands, such as the method of carrying out immobilizing processing of the electrolyte paint which dissolved polymer in the electrolysis solution beforehand as a method of forming a gel electrolyte, and the method of making carry out crosslinking reaction of the electrolyte paint which made the electrolysis solution contain a polymerization nature gelling agent, and using as a non fluidity electrolyte, are employable. In performing the paint which made the electrolysis solution contain a polymerization nature gelling agent for formation of a gel electrolyte by the method of carrying out crosslinking reaction, it prepares a paint by performing polymerization, such as ultraviolet curing and heat curing, by adding to an electrolysis solution by making into a polymerization nature gelling agent the ingredient used as the monomer which forms polymers.

[0064]As a polymerization nature gelling agent, what has unsaturated double bonds, such as an acrylyl group, a methacryloyl group, a vinyl group, and an allyl group, for example is mentioned. Specifically, for example Acrylic acid, methyl acrylate, ethyl acrylate, Ethoxyethyl acrylate, methoxy ethyl acrylate, ethoxyethoxyethyl acrylate, Polyethylene-glycol monoacrylate, ethoxyethyl methacrylate, Methoxy ethyl methacrylate, ethoxyethoxyethyl methacrylate, Polyethylene-glycol-monomethacrylate, N, and N-diethylamino ethyl acrylate, N and N-dimethylamino ethyl acrylate, glycidyl acrylate, Allyl acrylate, acrylonitrile, N-vinyl pyrrolidone, diethylene glycol diacrylate, Triethylene glycol diacrylate, tetraethylene glycol diacrylate, Polyethylene-glycol diacrylate, diethylene-glycol dimethacrylate, Triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, Polyethylene glycol dimethacrylate, polyalkylene glycol diacrylate, polyalkylene glycol dimethacrylate, trimethylolpropanalkoxy RETOTORI acrylate, These which can illustrate pentaerythritol alkoxy RETOTORI acrylate, pentaerythritol alkoxylate tetraacrylate, ditrimethylol propane alkoxylate tetraacrylate, etc. can use two or more sorts together. diacrylate and doria which contain two or more ethylene oxide groups preferably especially in these -- it is KURIRETO. Although the content in particular of the polymerization nature gelling agent in an electrolysis solution is not restricted, it is 1 % of the weight or more preferably. If content is low, the formation efficiency of polymers will fall and it will become difficult to carry out immobilizing of the electrolysis solution. On the other hand, since remains of an unreacted monomer and the operativity as an electrolyte paint will worsen if too large, it may usually be 30 or less % of the weight.

[0065]When making it form by the method of carrying out immobilizing of the electrolyte paint which contained polymer for the gel electrolyte beforehand, it is preferred to use as polymer the polymers which dissolve in an electrolysis solution at an elevated temperature, and form a gel electrolyte at ordinary temperature. That is, it is considered as a gel electrolyte by making into ordinary temperature the polymer which dissolved in the electrolysis solution at the elevated temperature. As a temperature at the time of an elevated temperature, 50-200 \*\* is usually 100-160 \*\* preferably. The stability of a gel electrolyte falls that it seems that it dissolves at low temperature too much. If a melting temperature is too high, decomposition of an electrolyte component, polymer,



etc. can be caused. Forced cooling can also be carried out although it is preferred as the method of immobilizing to allow an electrolysis solution to stand at a room temperature. Polymer which has rings, such as polyvinyl pyridine and Poly N-vinyl pyrrolidone, as polymer which can be used, for example; Poly methyl methacrylate, Ethyl polymethacrylate, butyl polymethacrylate, poly(methyl acrylate), Acrylic derivative system polymer, such as ethyl polyacrylate, polyacrylic acid, polymethacrylic acid, and polyacrylamide; Polyvinyl fluoride, Fluororesin, such as polyvinylidene fluoride; CN basis content polymer; polyvinyl acetate, such as polyacrylonitrile and a polyvinylidenecyanide, Polyvinyl alcohol system polymer, such as polyvinyl alcohol; containing halogen polymer, such as polyvinyl chloride and a polyvinylidene chloride, etc. are mentioned. Poly methyl methacrylate, polyacrylonitrile, polyethylene oxide, or those denaturation objects are preferably used in these. The mixture of the above-mentioned polymer, a conversion object, a derivative, a random copolymer, an alternating copolymer, a graft copolymer, a block copolymer, etc. can also be used.

[0066]The ranges of the weight average molecular weight of these polymer are 10,000–5,000,000 preferably. If a molecular weight is low, it will become difficult to form gel, and if another side and a remainder molecular weight are high, viscosity will become high too much and handling will become difficult. In the method of forming these gel electrolytes, since the method of making carry out crosslinking reaction of the electrolyte paint which made the electrolysis solution contain a polymerization nature gelling agent, and using as a non fluidity electrolyte becomes inter-electrode adhesion improves and especially remarkable [ the effect of this invention ], it is desirable.

[0067]In an electrolyte, various kinds of additive agents can be added if needed for the improved efficiency of a cell. As an additive agent which makes such a function reveal, Although limitation in particular is not carried out, trifluoro propylene carbonate, 1,6-dioxo spiro[4,4] nonane- 2,7-dione, 12-crown 4-ether, vinylene carbonate, catechol carbonate, a succinic anhydride, etc. are mentioned.

[0068]An electrolyte layer makes an electrolyte usually come to be impregnated into the spacer which consists of porous sheets. A spacer is the porous film provided between the anode and the negative electrode, isolates these and it supports an electrolyte layer. As a material of a spacer, polymers, such as polyolefines, such as polyethylene and polypropylene, polyolefines by which some or all of these hydrogen atoms was replaced with the fluorine atom, polyacrylonitrile, and polyaramide, can be mentioned. Preferably, they are polyolefine and the polyolefines by which fluoride substitution was carried out. Specifically, polyethylene, polypropylene, PORITETO truck fluoroethylene, polyvinylidene fluoride, etc. can be mentioned. Of course, they may be a copolymer containing the monomer unit of the above-mentioned polymer, and a mixture of polymer. A spacer may be the oriented film formed by 1 axis extension and biaxial extension, and may be a nonwoven fabric. 100 micrometers or less of thickness [ 50 micrometers or less of / 30 micrometers or less of ] of a spacer are usually 20 micrometers or less most preferably still more preferably. When thickness is too large, it is in the tendency for the rate characteristic and volume energy density of a cell to fall. Since cutting tends to become difficult by rigidity insufficiency and it is easy to produce a short circuit when too thin, not less than 7 micrometers is not less than 5 micrometers usually not less than 8 micrometers still more preferably preferably. The voidage of a spacer is usually 45–75% preferably 45 to 90%. If voidage is too large, mechanical strengths run short, and when too small, it is in the tendency for the rate characteristic of a cell, etc. to fall.

[0069]

[Example]Hereafter, although this invention is explained still in detail based on an example, this invention is not limited at all by the following example, in the range which does not change the gist, can be changed suitably and can be carried out. It shows a weight section that it is especially with a "part" in the following explanation, unless it refuses.

90 copies of example of anode manufacture 1 cobalt acid lithium, five copies of acetylene black, five copies of polyvinylidene fluorides, and 80 copies of N-methyl-2-pyrrolidone were kneaded with the



kneading machine for 2 hours, and it was considered as the anode paint 1.

[0070]Next, the anode paint 1 was applied by die coating of the extrusion die on the aluminum collector substrate of 20-micrometer thickness, it dried, and the active material layer which consists of a porous membrane with which the active material was bound on the charge collector with the binder was made to form. Subsequently, using the roll press (calendar), after consolidation, it cut and was considered as the anode 1.

90 copies of example graphite of negative-electrode manufacture (particle diameter of 15 micrometers), ten copies of polyvinylidene fluorides, and 100 copies of N-methyl-2-pyrrolidone were kneaded with the kneading machine for 2 hours, and were made into the negative-electrode paint 1.

[0071]Next, the negative-electrode paint 1 was applied by die coating of the extrusion die on the copper charge collector substrate of 20-micrometer thickness, it dried, and the active material layer which consists of a porous membrane with which the active material was bound on the charge collector with the binder was made to form. Subsequently, using the roll press (calendar), after consolidation, it cut and was considered as the negative electrode 1.

Ethylene carbonate containing  $\text{LiPF}_6$  of example of electrolyte paint creation 11 M concentration, Propylene carbonate and 925 copies of mixed liquor of phenyl ether (ethylene carbonate: volume ratio; propylene carbonate : phenyl ether = 7.3:7.3:1), 44 copies of tetraethylene glucol diacrylate, and polyethylene oxide -- doria -- the mixed stirring dissolution of 22 copies of KURIRETO, two copies of polymerization initiators, and nine copies of additive agents (succinic anhydride) was carried out, and it was considered as the electrolyte paint 1.

Apply the electrolyte paint 1 to the example 1 anode 1 and the negative electrode 1, and after laminating on both sides of the porosity film made from polyethylene independently dipped in the electrolyte paint 1 in between, immobilizing of the electrolyte is carried out by heating at 90 \*\* for 10 minutes, An anode and a negative electrode as shown in drawing 9, and the plate-like unit battery element which has an immobilizing nature electrolyte were created.

[0072]The terminal area of anodes and negative electrodes was bundled after laminating the obtained unit battery element, and the lead which takes out current to each terminal area was connected. Then, the laminate film with a thickness of about 100 micrometers which has a resin layer to both sides of an aluminum layer was accommodated in a sheathing material like drawing 9 which carried out opposite shaping. Then, the joining piece part (equivalent to the joining piece part 4A in drawing 5) except the neighborhood which took out the lead for the laminate film after enclosure with the vacuum seal was bent so that an entire-covering part might be met. The cell capacity of the flat cell A created in this way was 650mAh.

[0073]In the flat cell A created as mentioned above, it is 3 cycle \*\*\*\*\* about the charge and discharge between nominal working voltage at the constant current of 0.65A. This cell was inserted into assembling-die metal member holding like drawing 22 which adjusted opening height with the screw to 110% of the total thickness of the cell, and the overcharge examination was done. Upper limit voltage is set as 10V, and that is, charging a cell by the constant current of 1.8C (1.17A) from a discharge state was continued for 200 minutes. The thickness of the cell of a discharge state was 3.9 mm (the thickness of an electrode is 3.7 mm). Disclosure of the gas at the time of overcharge was not observed at all, but the maximum temperature of the battery surface was 94 \*\*. It was a grade in which most bulging of the cell by gas is not observed by the cell after overcharge, but a cell loosens slightly. The thickness of the cell after overcharge was 4.2 mm (the thickness of an electrode is 4.0 mm). Even if such a cell applied the pressure to the cell after overcharge, disclosure of the gas by the tear of a sheathing material was not observed.

[0074]As a result of inserting the flat cell A into member holding by the same method as the above, setting upper limit voltage as 10V and continuing charging a cell for 120 minutes by the constant current of 1.95A from a discharge state, disclosure of the gas at the time of overcharge was not observed at all, but the maximum temperature of the battery surface was 132 \*\*. It was a grade in which most bulging of the cell by gas is not observed by the cell after overcharge, but a cell loosens

slightly. The thickness of the cell after overcharge was 4.3 mm (the thickness of an electrode is 3.8 mm). Even if such a cell applied the pressure to the cell after overcharge, disclosure of the gas by the tear of a sheathing material was not observed.

a reference example -- the flat cell A (15 cm of monotonous each one product <sup>2</sup>) created as mentioned above -- the constant current of 0.65A -- the charge and discharge between nominal working voltage -- 3 cycle \*\*\*\*\*. The thickness of the cell of a discharge state was 3.9 mm (the thickness of an electrode is 3.7 mm). Next, upper limit voltage being set as 10V, and charging a cell by the constant current of 1.8C (1.17A) from a discharge state by the method to which load is applied according to bulging of a cell was continued for 200 minutes. As a result, bulging of the cell by gas was not observed at all by the cell after overcharge, but the thickness of the cell after overcharge was 4.6 mm (the thickness of an electrode is 4.3 mm). Under the present circumstances, the maximum load applied to the cell was 8.3 kg ( $8.3/15=0.55 \text{ kg/cm}^2$ ). The maximum temperature of the battery surface in this case was 85 \*\*.

The overcharge examination of the cell A was done on comparative example 1 member holding like Example 1 except not having accommodated the flat cell A.

[0075]As a result, the cell blistered during overcharge, it fumed 72 minutes afterward, and disclosure of the gas at the time of overcharge was observed. The maximum temperature of the battery surface in that case was 140 \*\*. Upper limit voltage was set as 10V on the same conditions, and as a result of continuing charging a cell by the constant current of 1.95A from a discharge state, the cell ignited 38 minutes afterward. From a reference example, by applying the pressure of specification (more than  $0.5 \text{ kg/cm}^2$ ) on a cell at the time of overcharge shows that the safety of the cell at the time of overcharge can be improved. That is, if member holding is designed so that the power which is equivalent to this load at the time of overcharge may be added, it turns out that the safety at the time of overcharge improves. If Example 1 is compared with the comparative example 1, the safety at the time of overcharge will actually improve by storing a cell to member holding so that a pressure may be added at the time of overcharge.

[0076]

[Effect of the Invention]In this invention, the peculiar problem in connection with the safety at the time of overcharge is solved, and bulging of the cell at the time of overcharge is controlled.

Therefore, the disclosure of poisonous gas, such as corrosion of a use device and organic gas, by damage and generating gas of the use device at the time of overcharge is prevented, and the rechargeable battery which raised the safety of the cell can be provided.

Therefore, the rechargeable battery which has an essential safety feature is realized, and even if it does not take other measures against overcharge, it can be considered as a relative more safe rechargeable battery. It can be considered as a safer lithium secondary battery by using together with other measures against overcharge.

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[Translation done.]

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TECHNICAL FIELD

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[Industrial Application]This invention relates to the rechargeable battery whose safety at the time of overcharge improved in detail about a rechargeable battery.

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PRIOR ART

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[Description of the Prior Art]Danger, such as ignition according [ the developed lithium secondary battery of high energy density ] to the height of the energy density, therefore the misuse of a cell, failure of a use device, etc. and emitting smoke, is increasing in recent years. In the present cell design high-energy-density-ized more, reservation of the safety of a rechargeable battery is one of the indispensable technical problems from such a background.

[0003]Especially in safety reservation of a cell, the safety reservation to a surcharge is one of the important technical problems. It is because this has the relatively high danger of a cell being in an overcharging condition, and an internal short circuit etc. happening as a result, and leading to accidents, such as emitting smoke of a cell, and ignition, with the rise of battery temperature when charging a rechargeable battery and the electrical and electric equipment more than predetermined flows by a certain cause. For example, generally, if a lithium secondary battery will be in an overcharging condition, generating of gas will take place by disassembly of an electrolysis solution etc. first. When the generation of gas arises, when this state continues, it not only leads to the burst of a cell, a liquid spill, etc., but battery temperature may rise eventually and it may lead to accidents, such as emitting smoke and ignition.From such a viewpoint, various prevention methods for a surcharge have so far been proposed.

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EFFECT OF THE INVENTION

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[Effect of the Invention]In this invention, the peculiar problem in connection with the safety at the time of overcharge is solved, and bulging of the cell at the time of overcharge is controlled. Therefore, the disclosure of poisonous gas, such as corrosion of a use device and organic gas, by damage and generating gas of the use device at the time of overcharge is prevented, and the rechargeable battery which raised the safety of the cell can be provided. Therefore, the rechargeable battery which has an essential safety feature is realized, and even if it does not take other measures against overcharge, it can be considered as a relative more safe rechargeable battery. It can be considered as a safer lithium secondary battery by using together with other measures against overcharge.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention]It is known as a method with the common mechanical current cutoff method by the safety valve using the gas emitted by disassembly of the control method by the electronic circuit attached to the battery exterior, the electrolysis solution at the time of overcharge, etc. as the concrete method of a overcharge preventive measure, etc. However, in such a method, an electronic circuit and a safety valve are carried in a cell, and also [ required ] there was a problem that cell cost went up and restrictions of the design of a cell arose.

[0005]In recent years, a plate-like case is constituted using a lightweight sheathing material like the laminate film which provides a resin layer in both sides of a gas barrier layer, and the cell of the type which seals the battery element which has an anode and a negative electrode in this is developed. Since a lightweight film can be used for such a cell as a sheathing material, it has some advantageous points compared with the case which consists of conventional metal. That is, since the composition of a case is simpler compared with the case where the case which it not only can miniaturize, but consists a cell of a light weight and a metal can containing an electronic circuit and a safety valve more is used, becoming in cost and advantageous is also expected. On the other hand, in such a cell, the control method by the above-mentioned electronic circuit and the mechanical current cutoff method by a safety valve have the problem of a cell case of being constitutionally especially difficult.

[0006]The method by the shutdown which, on the other hand, used fusion of the separator by the rise in heat of a cell as the concrete method of a overcharge preventive measure, By adding the overcharge inhibitor which has oxidation potential in electropositive potential from the anode potential at the time of a full charge to an electrolysis solution, when anode potential rises by an overcharging condition, how to trigger oxidation reaction of organic additives and inhibit the run away reaction in a cell at the time of overcharge is also known. However, since the shutdown method by the former separator has the rapid run away reaction at the time of overcharge, it is sometimes difficult to make it fully function as overcharge protection. In order to add the overcharge inhibitor which does not necessarily participate in the charge and discharge of a cell directly to an electrolysis solution in the latter method, have an adverse effect on battery capacity, or, Or gas is emitted as a result of oxidation reaction of the overcharge inhibitor at the time of overcharge, and we are anxious about the disclosure of poisonous gas, such as corrosion of a use device, and organic gas, by this generating gas, etc.

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## MEANS

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[Means for Solving the Problem]As a result of repeating examination wholeheartedly that this invention persons should attain the above-mentioned purpose, generating of gas within a cell at the time of overcharge, It can control, if pressure more than specification which is in inter-electrode at the time of overcharge is added, And breakage and corrosive gas from a cell of a use device by bulging of a cell when generating of gas of a cell at the time of overcharge is controlled, Since a rise of battery temperature was also controlled, it found out that emitting smoke of a cell and danger to ignition could be reduced further, and it not only can prevent disclosure of toxic gas, but completed this invention.

[0008]That is, a gist of this invention consists below.

(1) In member holding which accommodates a lithium secondary battery which a plate-like case where a battery element which has an anode, a negative electrode, and an electrolyte consists of sheathing materials comes to store, Member holding for lithium secondary batteries characterized by vertical intensity being the intensity which can bear a pressure more than  $0.5 \text{ kg/cm}^2$  to a monotonous side of the above-mentioned case.

(2) Member holding for lithium secondary batteries of (1) whose height of a seat part of member holding is 101 to 120% of the total thickness of a lithium secondary battery.

A secondary battery pack which accommodates a lithium secondary battery which a plate-like case where a battery element which has an anode, a negative electrode, and an electrolyte becomes an inside of member holding of (3), (1), or (2) from a sheathing material comes to store.

(4) A secondary battery pack given in (3) whose thickness of a sheathing material is 0.2 mm or less.

(5) A secondary battery pack of (3) - (4) whose thickness of a lithium secondary battery is not less than 2 mm.

(6) A secondary battery pack of (3) - (5) whose nominal capacity of a cell is 100 or more mAh.

(7) A secondary battery pack of (3) - (6) in which a sheathing material consists of a laminate film in which a synthetic resin layer and a gas barrier layer were laminated.

(8) A secondary battery pack of (3) - (7) in which a battery element has a non fluidity electrolyte between an anode and a negative electrode.

[0009]

[Embodiment of the Invention]Hereafter, it explains per embodiment of this invention. The typical exploded perspective view of the member holding which requires drawing 18 for one embodiment of this invention, and drawing 19 are the A-A arrowed cross-section figures of drawing 18 showing signs that the battery element was stored by member holding. It may write for convenience among a figure a thickness direction [ the direction which shows the direction which shows the direction shown by x by a longitudinal direction and y by a cross direction and z ].

[0010]The member holding 181 consists of the barrel 181a and the two lids 181b and 181c. The barrel 181a is an open tube-like object which has an upper face part, an undersurface part, the front part, and a back part, and has the plate-like rectangular parallelepiped shape which spreads in a xy



plane as a whole. The barrel 181a is the really molded member made of resin. The barrel 181a has a seat part (space part) which carries out an opening outside in the longitudinal direction in a figure. The lids 181b and 181c are the members made of resin of the flat plate shape which spreads in the yz direction, respectively, adhere with the barrel 181a in respect of the right and left of the barrel 181a, and isolate a seat part with the exterior. The barrel 181a and the lids 181b and 181c are screwed with the screw thread 182, respectively. The terminal area 182 connected with the anode of a battery element and the negative electrode is formed in the lid 181c.

[0011]A battery element is stored by the seat part. A battery element carries out two or more (in this case, 3) laminations of the unit battery element which laminates the anode 192a and the negative electrode 192b via the electrolyte layer (spacer) 193c in the above-mentioned laminating direction. A battery element has the flat plate shape which spreads in the xy direction as a whole. The vacuum lock of the battery element is carried out to the case which consists of the sheathing materials 191a and 191b of two sheets.

[0012]In this invention, more than  $0.5 \text{ kg/cm}^2$  makes preferably intensity of said member holding 181 of a vertical direction (in drawing 19, it is thickness direction z) more than  $0.6 \text{ kg/cm}^2$  to the monotonous side of the above-mentioned case which spreads in the xy direction. The yield of the gas by the decomposition reaction of the electrolysis solution which will press an electrode by a moderate pressure by member holding at the time of such strong \*\*\*\*\* for member holding and overcharge, and, as a result, serves as a trigger of the run away reaction of the cell at the time of overcharge can be decreased remarkably. Under anticipated-use conditions, since load inter-electrode [ this ] may lead to evils, such as a short circuit of a cell, it is preferred to design member holding so that pressure may be added to inter-electrode in an overcharging condition. That is, at the time of overcharge, especially the thickness of an electrode increases notably from near the charge depth which the dedope of the lithium ion from an anode ends. Therefore, as for member holding, when this phenomenon is used, it is considered as the thickness of member holding which does not press an electrode at the time of anticipated use and an electrode blisters at the time of overcharge, it is preferred to consider it as the thickness of member holding which sticks to a cell, and stops bulging, namely, presses a cell. It is preferred to specifically make the height ( $L_2$  shows drawing 19) of the seat part of member holding into 101 to 120% of the total thickness ( $L_1$  shows drawing 19) of a lithium secondary battery in consideration of there being bulging of few cells with charging a cell under an anticipated-use condition.

[0013]Since what has the above-mentioned, too much large intensity of member holding is actually difficult to get, below  $50 \text{ kg/cm}^2$  usually makes [ below  $100 \text{ kg/cm}^2$  ] it desirable. The above-mentioned intensity of member holding is controllable by material, its attachment intensity, etc. of member holding. In the above-mentioned example, although the member holding 181 used the thing made of resin, the material in particular is not limited, for example, it can use various kinds of materials, such as a hybrid of metal, and resin and metal. In the above-mentioned example, although the barrel 181a and the lids 181b and 181b were attached with the screw thread, it is not limited in particular, for example, it can stop with adhesives or adhesive tape, or can fix with a nail.

[0014]In the above-mentioned example, although what consists of the barrel 181a and the lids 181b and 181b was used for the member holding 181, In addition, the member holding which consists of the barrel 181a and the lid 181b of the owner bottom which carries out an opening only to one side as shown, for example in drawing 20, The member holding which consists of the barrel 181a and the lid 181b of the owner bottom which carries out an opening to the upper part (thickness direction) as shown in drawing 21, and the member holding which supports the plate shaped member 184a of an up-and-down couple as shown in drawing 22 with the leg object 185 of plurality (in this case, 4) can be used. Also in these cases, the barrel 181a and the lid 181b are \*\*\*\*\*ed, and are attached with a nail, adhesives, adhesive tape, etc.

[0015]The secondary battery pack in which the member holding 181 comes to store a battery

element is usually used, being connected to other cell use devices. As such a cell use device, a cellular phone, a personal digital assistant, portable audio equipment, A cordless phone cordless handset, a cell book player, a pager, a handy terminal, Portable fax, a portable copy, a portable printer, a headphone stereo, A video movie, a liquid crystal television, a handy cleaner, portable CD, Various kinds of apparatus, such as medical equipment, such as an electrical machinery shaver, an electronic translating machine, a car telephone, a transceiver, a power tool, an electronic notebook, a calculator, memory card, a tape recorder, radio, a backup power supply, a camera, a pacemaker, and hearing aid, can be mentioned. Various kinds of functions (a circuit, a driver, etc.) are attached in a battery pack, and the battery pack itself can also be made into a cell use device.

[0016]Next, the lithium secondary battery stored by member holding is explained. When the lithium secondary battery used by this invention has too thin the thickness of the whole lithium secondary battery which the plate-like case where the battery element which has an anode and a negative electrode consists of sheathing materials comes to store, since there are few yields of the gas at the time of overcharge relatively, Especially especially in the case of not less than 2 mm, the effect of this invention is remarkable 1 mm or more. Since it miniaturizes and is hard to carry out the weight saving of the cell, 4 mm or less is of 5 mm or less usually on the other hand too much thick still more preferably 4.5 mm or less preferably.

[0017]Since the cell with small capacity of a cell has relatively few yields of the gas at the time of overcharge, 100 or more mAh of lithium secondary batteries in 200 or more mAh are usually preferably used for it as nominal capacity. A battery element has an anode and a negative electrode. There is no restriction in particular in the shape of a battery element, and various kinds of shape which can be stored in a plate-like case can be adopted. For example, the monotonous lamination type shape which carries out two or more (in this case, 3) laminations of the plate-like unit battery element which laminates the anode 192a as shown in drawing 19, and the negative electrode 192b via the electrolyte layer (spacer) 193c as a battery element in the above-mentioned laminating direction is employable. The winding mold configuration which winds the band-like layered product which laminated the anode and the negative electrode via the electrolyte layer is also employable.

[0018]The lithium secondary battery by which sealing storage was carried out with the sheathing material of film state in the battery element which laminates hereafter two or more plate-like unit battery elements which have an anode, a negative electrode, and a non fluidity electrolyte layer to a thickness direction is made into an example, and is explained to details per embodiment of a lithium secondary battery. The exploded perspective view of the cell which requires drawing 1 for an embodiment, and drawing 2 The sectional view of the important section of this cell, It is a typical sectional view showing signs that the perspective view of a cell blisters, as for the perspective view with rough drawing 3, drawing 4, and drawing 5 of a battery element, the sectional view ((a) is a whole sectional view and (b) is an expanded sectional view of B portion of (a)) of a case blisters, as for drawing 6, and a cell blisters, as for drawing 7. A cell given in the expedient top of explanation and drawing 1 is carried out for upside down, and it is shown in drawing 4 and drawing 5.

[0019]After this cell accommodates the battery element 1 in the crevice of the sheathing material 3, it pours in the insulating materials 5, such as an epoxy resin and an acrylic resin, near the terminal area (tabs 4a and 4b) of the battery element 1, puts the sheathing material 2 on the sheathing material 3 after that, and joins the edge parts 2a and 3a of the sheathing materials 2 and 3 by a vacuum lock. The sheathing material 2 is plate-like as drawing 1. The sheathing material 3 is a thing of the shape of a shallow non-lid box with the seat part 3b which consists of a crevice of rectangular case shape, and the edge part 3a jutted out of four peripheries of this seat part 3b over flange shape at the method of outside.

[0020]The battery element 1 laminates two or more unit battery elements to a thickness direction as drawing 3. From this unit battery element, the tab 4a or 4b is pulled out. Each tab 4a from an anode is bundled (that is, pile up mutually and be put together), the positive electrode lead 21 is joined, and the positive pole terminal part is formed. Tab 4b from a negative electrode is bundled,

the negative electrode lead 21 is joined, and the negative pole terminal part is formed.

[0021]After the battery element 1 is accommodated in the seat part 3b of the sheathing material 3, the insulating material 5 is poured in the tab 4a and near the 4b and the battery element side a positive pole terminal part and near the negative pole terminal part is covered with an insulating material, the sheathing material 2 is put. One pair of leads 21 which extended from the battery element 1 are pulled out outside through the edge part 2a of one side part of the sheathing materials 2 and 3, and the mating face of 3a, respectively. Then, the edge part 2a of four peripheries of the sheathing materials 2 and 3 and 3a are airtightly joined by techniques, such as thermo compression bonding and ultrasonic welding, under decompression (preferably vacuum) atmosphere, and the battery element 1 is enclosed in the sheathing material 2 and 3. Then, curing treatment is presented with the insulating material 5 by heating etc., and the insulating material 5 adheres thoroughly near the terminal area. Since the sheathing material is closed before adhering thoroughly, the shape of a cell hardly changes at the time of adherence.

[0022]The case which consists of the sheathing materials 2 and 3 is constituted by joining the edge part 2a and 3a. This case is provided with the following as shown in drawing 4.

The entire-covering part 4B of the approximately rectangular parallelepiped shape which wraps the battery element 1 entirely by side wall part 4B<sub>1</sub>, raised bottom part 4B<sub>2</sub>, and a lower base part (not shown).

The edge part 2a of said sheathing material, the joining piece parts 4A, 4F, and 4G to which it comes to join 3a.

[0023]In the state given in drawing 4, the above-mentioned joining piece parts 4A, 4F, and 4G are jugged over the method of outside out of side wall part 4B<sub>1</sub> of the entire-covering part 4B which has wrapped the battery element 1 entirely. Then, as shown in drawing 5, among these joining piece parts, the joining piece parts 4A and 4G are bent so that side wall part 4B<sub>1</sub> of the entire-covering part 4B may be met, and the thing (it fixes) stick to side wall part 4B<sub>1</sub> of the entire-covering part 4B with adhesives is made. That is, for example, as shown in drawing 6, the joining piece part 4A is bent along with side wall part 4B<sub>1</sub> of the entire-covering part 4B, and these are mutually pasted up with the adhesives 51. As the adhesives 51, various kinds of things, such as epoxy adhesive, acrylic adhesives, urethane system adhesives, hot melt system adhesives, and synthetic rubber system adhesives, can be used. Of course, two or more adhesives can also be used together. In order to control the fixing strength of a joining piece part and a side wall part, in selection of adhesives, it is necessary to take into consideration the construction material of the surface of a joining piece part and a side wall part, the environment at the time of fixing work (humidity, temperature, etc.), etc. but, and. Preferably, cure time is short and uses the hot melt system adhesives easily hardened under the low environment of the dew point used in the case of manufacture of a nonaqueous cell.

[0024]Thus, as for these joining piece parts, although it can adhere to side wall part 4B<sub>1</sub> in at least a part of joining piece part (joining piece parts 4A and 4G), adhering with predetermined fixing strength is preferred in this case. That is, when the following fixing strength examination is done, said joining piece part adheres 20 degrees or less still more preferably 30 degrees or less by the intensity of the grade which can maintain the angle of 10 degrees or less most preferably preferably 45 degrees or less to said entire-covering part.

Charging the cell which has fixing strength testing cell voltage in 3V with the current of 1.8C is continued for 200 minutes in the range which set upper limit voltage to 10V. However, 1C is a current value for discharging the capacity charged and obtained in 1 hour until a current value is set to 0 from the cell voltage 2.7V with 4.2V constant voltage. The angle of the flat surface where the angle of the joining piece part and entire-covering part in the portion which adhered includes the adhesion side of a joining piece part, and a flat surface including the adhesion side of an entire-

covering part to make (in drawing 6, it is an angle of S1 and S2 to make.) In this case, it is a thing on account of [ zero ] parallel.

[0025]Generally, a cell tends to blister in an overcharging condition. Namely, as shown in drawing 7 at the time of overcharge, a cell tends to blister in the direction P. In this invention, a battery element is accommodated in the member holding of said predetermined intensity so that bulging to this direction P may be prevented. As a result, a safer cell can be provided in an overcharging condition. This will prevent effectively bulging generated the first stage at the time of overcharge, and is presumed to have inhibited the run away reaction of the cell after it.

[0026]In the above example, although the joining piece parts 4A and 4G have adhered to side wall part 4B<sub>1</sub> with adhesives, they are not limited to the method of adherence using adhesives. For example, a joining piece part can be made to adhere to an entire-covering part using adhesive tape.

[0027]In the above-mentioned example, although the joining piece parts 4A and 4G are bent only once along with side wall part 4B<sub>1</sub>, For example, the joining piece part 4A is bent further once again on the way, and it may be made to make the tip of the joining piece part 4A intervene between the joining piece part 4A and side wall part 4B<sub>1</sub>, as shown in drawing 8. Thus, by carrying out two or

more diffraction music of the joining piece part, air etc. can be prevented from invading from the side of a joining piece part, or the mechanical strength in a side wall part can be raised further.

[0028]At drawing 1, although the sheathing materials 2 and 3 serve as a different body, by this invention, the sheathing materials 2 and 3 may serve as series one like drawing 9. In drawing 9, one side of the sheathing material 3 and one side of the sheathing material 2 stand in a row, and the sheathing material 2 serves as the shape of a lid which stands in a row turnable to the sheathing material 3. The crevice of the seat part 3b is formed, and except that the joining piece part is not formed in this one side, it becomes a thing of the same composition as a joining piece part from one side with which these sheathing materials 2 and 3 are connected. Also in the case of this drawing 9, the joining piece parts 4A and 4G adhere to side wall part 4B<sub>1</sub> with adhesives.

[0029]Although the sheathing material 3 with the seat part 3b and the plate-like sheathing material 2 are shown by drawing 1 and 9, In this invention, the battery element 1 may be entirely wrapped like drawing 10 with the sheathing materials 6 and 7 with the shallow box-like seat parts 6b and 7b and the edge parts 6a and 7a juttied out of four peripheries of these seat parts 6b and 7b, respectively. In drawing 10, although the sheathing materials 6 and 7 serve as a series object, these may serve as a different body like said drawing 1.

[0030]In drawing 1 and 9 or 10 composition, since the seat part of the battery element is formed beforehand, a battery element can be accommodated more in a compact, and the accommodation itself is easy. In the above-mentioned explanation, after accommodating a battery element in a seat part, the insulating material is poured in near the terminal area, but an insulating material adheres and flows between the mating face of an edge part, a battery element, and a sheathing material in this case, and junction of an edge part may be checked or it may not become the cell shape as a design. Then, after supplying an insulating material near the terminal area of a battery element, the above-mentioned problem is avoidable by accommodating a battery element in a seat part. Since an insulating material cannot be supplied to the abbreviated upper half of a battery element even if especially in the case of drawing 10 it supplies an insulating material after accommodating a battery element, this manufacturing method is preferred. On the other hand, in this method, since the handling in the state where the insulating material was supplied needs to carry the battery element which is not easy and needs to arrange to a sheathing material, cautions are required for the handling at the time of manufacture. It can be said that the former method is preferred in this point.

[0031]In this invention, turn up the sheet shaped flat sheathing material 8 of one sheet in the shape of 2 Thu chip boxes along with the central neighborhood 8a like drawing 11, and two pieces with 8B are formed the 2nd piece with 8A the 1st piece, These 1st pieces of the battery element [ the 2nd piece of ] 1 is made to intervene between 8B with 8A, like drawing 12, piece [ 1st ] edge part 8b

[ piece / 2nd ] of 8B may be joined to 8A, and the battery element 1 may be enclosed. Also in this case, the joining piece parts 4A and 4G adhere to side wall part 4B<sub>1</sub> of the entire-covering part which wraps the battery element 1 entirely with adhesives. Since a joining piece part is made to meet an entire-covering part, it bends and it is fixing with adhesives or adhesive tape further even if it is in the cell constituted in this way, the blister of the battery element in the early stages of a surcharge can be effectively prevented also in this case, and the intensity of the side of a cell and rigidity are high. Of course, the bent joining piece part is prevented also from deserting an entire-covering part. Since the intensity of the side of a cell and rigidity are high, peeling is prevented from arising by the active material even when shocked by the side.

[0032]Although the joining piece parts 4A and 4G have adhered to side wall part 4B<sub>1</sub> of the entire-covering part 4B, they can also make it adhere to portions other than a side wall part in the above example. For example, as shown in drawing 17, where the lead 21 is pulled out, wrap entirely, so that the circumference of a battery element may be wound for the sheathing material 2 of one sheet, and the periphery of a sheathing material is joined. When the joining piece part 4F provided in the portion which pulled out the lead, the joining piece part 4G provided in that opposing side, and the joining piece part 4H provided over the upper surface 4I of an entire-covering part are made to form, this joining piece part 4H and the entire-covering part upper surface 4I can also be adhered with adhesives or adhesive tape.

[0033]In the above example, it fills up with the insulating material 5 near the terminal area (tabs 4a and 4b). As a result, the blister of the battery element in the early stages of a surcharge can be prevented effectively, and a short circuit is prevented further more effectively. As the insulating material 5, a synthetic resin is preferred, and although an epoxy resin, an acrylic resin, silicone resin, etc. are illustrated, since cure time is short, an epoxy resin or an acrylic resin is especially preferred. Since a possibility of having an adverse effect on battery capacity is low, especially an acrylic resin is the most preferred. An insulating material is supplied near the terminal area in the state that it does not harden and of being liquid, and adheres near the terminal area thoroughly by hardening. In drawing 1, as for the insulating material 5, although supplied separately, respectively, in order [ of a positive pole terminal part and a negative pole terminal part ] to improve the safety at the time of overcharge more, it is more preferred to cover the whole side of a battery element ranging from the positive pole terminal part to a negative pole terminal part. In covering of the battery element side near [ this ] the terminal area, it is preferred to form a larger spacer than these between an anode and a negative electrode, and to adhere mutually in the flash parts of this spacer especially.

[0034]That is, if it is in a battery element, as shown, for example in drawing 16, the spacer 13 made the anode 11 and the negative electrode 13 overflow a little, formed the flash part 13a, and has prevented the short circuit of the anode 11 and the negative electrode 13. Since a battery element is restrained by the laminating direction by adhering by an insulating material in these flash part 13a, even if it is at the overcharge time, bulging of a battery element is prevented, and the thermal run-away of a cell is prevented. Of course, an insulating material can be continued and supplied to the whole side of a battery element, and is preferred.

[0035]As for the sheathing material which stores a battery element, what has shape changeability is preferred. As a result, when a sheathing material is closed under a vacua, it can give the function which strengthens the inter-electrode lamination of a battery element, and, as a result, it is not only easy to create the cell of various shape, but can raise battery characteristics, such as a cycle characteristic. Since the volume energy density and weight energy density of a cell become larger as the thickness of a sheathing material is thin, since the intensity itself is relatively low, it is not only desirable, but the effect of this invention becomes remarkable especially. The thickness of a sheathing material is usually 0.15 mm or less preferably 0.2 mm or less. However, since insufficient strength becomes remarkable and becomes easy to penetrate moisture etc., 0.02 mm or more is

usually too much thin preferably 0.01 mm or more.

[0036]As a material of a sheathing material, metal, such as aluminum, iron which carried out the nickel plate, and copper, a synthetic resin, etc. can be used. Preferably, they are the laminate film in which the gas barrier layer and the resin layer were provided, and the laminate film in which the resin layer was especially provided in both sides of the gas barrier layer. Such a laminate film has high gas barrier property, and it has high shape changeability and thinness. As a result, thin-film-izing and the weight saving of a sheathing material can become possible, and the capacity as the whole cell can be raised.

[0037]As a material of the gas barrier layer used for a laminate film, metallic oxides, such as alloys, such as metal and stainless steel, such as aluminum, iron, copper, nickel, titanium, molybdenum, and gold, and Hastelloy, silicon oxide, and an aluminum oxide, can be used. Preferably, it is lightweight and is aluminum which is excellent in processability. As resin used for a resin layer, various kinds of synthetic resins, such as thermoplastics, thermoplastic elastomer, thermosetting resin, and a plastic alloy, can be used. That with which fillers, such as a filler, are mixed is also included in these resin.

[0038]As composition of a concrete laminate film, as shown in drawing 13 (A), that by which the gas barrier layer 40 and the resin layer 41 were laminated can be used. A desirable laminate film, As shown in drawing 13 (B), form the synthetic resin layer 41 for functioning as an outside protective layer in the lateral surface of the gas barrier layer 40, and. It is considered as 3 layered structure which laminated the synthetic resin layer 42 which functions as an inside protective layer for preventing contact with the corrosion and the gas barrier layer by an electrolyte, and a battery element to a medial surface, or protecting a gas barrier layer.

[0039]In this case, the resin used for an outside protective layer has the desirable resin which was preferably excellent in chemical resistance, such as polyethylene, polypropylene, denaturation polyolefine, an ionomer, amorphous polyolefin, polyethylene terephthalate, and polyamide, or a mechanical strength. As an inside protective layer, a chemical-resistant synthetic resin is used, for example, polyethylene, polypropylene, denaturation polyolefine, an ionomer, an ethylene-vinylacetate copolymer, etc. can be used.

[0040]The laminate film can also form the adhesive layer 43, respectively between the gas barrier layer 40, the synthetic resin layer 41 for protective layer formation, and the synthetic resin layer 42 for corrosion-resistant layer formation, as shown in drawing 14, and it is preferred. In order to paste up sheathing materials, the glue line which consists of resin which can be innermost welded [ of composite ], such as polyethylene and polypropylene, can also be provided further again. A case is formed using these metal, a synthetic resin, or composite. Shaping of a case may weld and form the circumference of a film like body, and may carry out draw forming of the sheet like body by vacuum forming, pressure forming, press forming, etc. It can also fabricate by carrying out injection molding of the synthetic resin. When based on injection molding, usually a gas barrier layer is formed of sputtering etc.

[0041]For providing beforehand, spinning etc. can perform the seat part which becomes a sheathing material from a crevice. As for a sheathing material, it is preferred that processing uses the thing of film state at an easy point. The battery element which has an anode, a negative electrode, and an electrolyte is stored in a case. As mentioned above, the battery element can wind the layered product (unit battery element) which consists of an anode, a negative electrode, and an electrolyte layer, can make it winding shape, and can also store this in a case, and can also store the above-mentioned layered product (unit battery element) in a case with flat plate shape as it is. Like the statement to said drawing 2 and 3, two or more unit battery elements can be laminated to a thickness direction, and it can also be considered as a battery element. The suitable composition of a unit battery element is explained below.

[0042]Drawing 15 shows an example with a preferred unit battery element which consists of this lithium secondary battery. This unit battery element laminates the negative electrode which consists of the anode, the spacer (electrolyte layer) 24, the negative electrode active material layer 25, and



the negative pole collector 26 which consist of the positive pole collector 22 and the positive active material layer 23. In order to control the deposit of a lithium dendrite, a negative electrode is made larger than an anode. In order to prevent a short circuit, the spacer 24 is made larger than an anode and a negative electrode. By making a spacer larger than positive and negative poles, it can adhere in both the flash parts of the spacer of a unit battery element as mentioned above.

[0043]Although two or more these unit battery elements are laminated and it is considered as a battery element, on the occasion of this lamination, the unit battery element of the order posture (drawing 15) which made the anode the upper part and made the negative electrode the bottom, and this laminate by turns the unit battery element of the reverse posture (graphic display abbreviation) which made the anode the bottom conversely and made the negative electrode the upper part. That is, the unit battery element which adjoins a laminating direction is laminated so that like poles (namely, anodes and negative electrodes) may meet.

[0044]The positive electrode tab 4a is installed from the positive pole collector 22 of this unit battery element, and the negative electrode tab 4b is installed from the negative pole collector 26. In drawing 15, although it has indicated that the \*\*\*\*\* positive active material layer and the negative electrode active material layer are formed in one side of a positive pole collector, and one side of a negative pole collector, of course, an active material layer can be formed in both sides of a charge collector. In this case, the active material layer by which the same charge collector of each other was formed in the opposite field can be made into the component of a unit battery element which differs mutually.

[0045]The plane shape of an electrode is arbitrary and can be made into a quadrangle, circular, a polygon, etc. The tabs 4a and 4b for lead combination are usually formed successively by the charge collectors 22 and 26 as drawing 15. When an electrode is a quadrangle, as usually shown in drawing 3, the tab 4a which projects from a positive pole collector near the side of one side of an electrode is formed, and the tab 4b of a negative pole collector is formed near the other side.

[0046]It is effective to laminate two or more unit battery elements, when attaining high capacity-ization of a cell, but in this case, each of the tab 4a from each unit battery element and the tab 4b is usually combined with a thickness direction, and the terminal area of an anode and a negative electrode is formed. As a result, it becomes possible to obtain the mass battery element 1. As shown in drawing 2, the lead 21 which consists of metal of a thin film integrated circuit is combined with the tabs 4a and 4b. As a result, the anode and negative electrode of the lead 21 and a battery element are combined electrically. Resistance welding of spot welding etc., ultrasonic welding, or laser welding can perform combination of tab 4a and 4b, and combination with the tabs 4a and 4b and the lead 21.

[0047]at least one lead 21 of the above-mentioned positive electrode lead and a negative electrode lead — it is preferably preferred as both leads to use annealing metal. As a result, it can be considered not only as intensity but as the cell which broke, bent and was excellent in endurance. Generally as a kind of metal used for a lead, aluminum, copper and nickel, SUS, etc. can be used. A material desirable as a lead of an anode is aluminum. Construction material desirable as a lead of a negative electrode is copper.

[0048]1 micrometers or more of thickness [ not less than 10 micrometers of / not less than 20 micrometers of ] of the lead 21 are usually not less than 40 micrometers most preferably still more preferably. When too thin, it is in the tendency for mechanical strengths of a lead, such as tensile strength, to become insufficient. 500 micrometers or less of thickness of a lead are of 1000 micrometers or less usually 100 micrometers or less still more preferably preferably. It is in the tendency to be in the tendency to bend and for endurance to get worse when too thick, and for closure of the battery element in a case to become difficult. The advantage by using the annealing metal later mentioned to a lead is so remarkable that the thickness of a lead is thick.

[0049]The exposure length to the exterior of a lead is usually 1 mm or more about 50 mm or less. As mentioned above, although a battery element may be a wound type cell which winds the layered



product (unit battery element) which laminated the anode and the negative electrode via the electrolyte layer, it is preferred to make a spacer intervene between an anode and a negative electrode also in this case, and to make this larger than positive and negative poles.

[0050] Hereafter, the material used for a lithium secondary battery is explained. A battery element usually has an anode, a negative electrode, and an electrolyte layer that exists among them. An anode and a negative electrode usually contain a charge collector and the active material layer provided on it. As a positive pole collector, although various kinds of metal, such as aluminum, nickel, and SUS, can be used, it is aluminum preferably. The thickness of a charge collector is not less than 5 micrometers still more preferably, and is of 1 micrometers or more usually 20 micrometers or less still more preferably 25 micrometers or less preferably of 30 micrometers or less usually not less than 3 micrometers. As thin, it is more desirable from a viewpoint of volume energy density and weight energy density, but the handling of too much thin one becomes difficult easily in respect of intensity etc. Charge collectors may be tabular [ like the usual metallic foil ], and mesh state like a punching metal. The surface roughening process of the surface of a charge collector can be carried out if needed.

[0051] As an active material which uses for an anode and can do things, it is considered as the compound which can occlusion emit a lithium ion, and an inorganic compound or an organic compound can also be used. As an inorganic compound, the oxide of transition metals, such as Fe, Co, nickel, and Mn, the multiple oxide of lithium and a transition metal, transition metal sulfide, etc. are mentioned. As a transition metal oxide, specifically  $\text{MnO}_2$  and  $\text{V}_2\text{O}_5$ ,  $\text{V}_6\text{O}_{13}$ ,  $\text{TiO}_2$  etc. can be illustrated, nickel acid lithium, cobalt acid lithium, manganic acid lithium, etc. can be illustrated as a multiple oxide of lithium and a transition metal, and  $\text{TiS}_2$ ,  $\text{FeS}$ , etc. can be illustrated as transition metal sulfide. As an organic compound, conductive polymers, such as poly aniline, etc. are mentioned, for example. The arbitrary methods of carrying out quantity mixing and using as positive active material are also suitably used in these arbitrary inorganic compounds and an organic compound. It is a multiple oxide which contains preferably the multiple oxide of lithium and a transition metal, at least one sort of transition metal oxides chosen from the group which consists of manganese, nickel, and cobalt especially, and lithium. Especially, the multiple oxide containing cobalt and lithium and the multiple oxide containing nickel and lithium are preferred. The particle diameter of positive active material is a point of battery characteristics, such as a rate characteristic and a cycle characteristic, and is usually 1–10 micrometers preferably 1–30 micrometers.

[0052] As a negative pole collector, although various kinds of metal, such as copper, nickel, and SUS, can be used, it is copper preferably. The thickness of a charge collector is not less than 5 micrometers still more preferably, and is of 1 micrometers or more usually 20 micrometers or less still more preferably 25 micrometers or less preferably of 30 micrometers or less usually not less than 3 micrometers. As thin, it is more desirable from a viewpoint of volume energy density and weight energy density, but the handling of too much thin one becomes difficult easily in respect of intensity etc. Charge collectors may be tabular [ like the usual metallic foil ], and mesh state like a punching metal. The surface roughening process of the surface of a charge collector can be carried out if needed.

[0053] As an active material which can be used for a negative electrode, various kinds of compounds which can occlusion emit lithium outside a lithium metal can be used. Specifically, carbon materials, such as lithium alloy; graphite, such as a lithium metal; lithium aluminum alloy, a lithium bismuth cadmium alloy, and a lithium \*\*\*\*- cadmium alloy, and corks, etc. can be mentioned. Oxides and lead sulfate, such as silicon, tin, zinc, manganese, iron, and nickel, can also be used. Since it is in the tendency for the safety at the time of overcharge to fall that it is especially easy to generate a dendrite in the case of charge when a lithium metal and a lithium alloy are used, carbon materials, such as graphite and corks, are preferred. The particle diameter of negative electrode active

material is a point of battery characteristics, such as initial efficiency, a rate characteristic, and a cycle characteristic, and is usually 15–30 micrometers preferably 1–50 micrometers.

[0054]The active material layer of an anode and a negative electrode usually contains a binder outside the above-mentioned active material. As a binder to be used, it needs to be stable to an electrolysis solution etc., and weatherability, chemical resistance, heat resistance, fire retardancy, etc. are desired. As a binder, silicate, an inorganic compound like glass, and various kinds of resin that mainly consists of polymers can be used. As resin, for example, alkane system polymer; polybutadienes, such as polyethylene, polypropylene, and Poly 1,1-dimethylethylene, Unsaturation system polymer, such as polyisoprene; Polystyrene, polymethylstyrene, Polymer which has rings, such as polyvinyl pyridine and Poly N-vinyl pyrrolidone; Poly methyl methacrylate, Ethyl polymethacrylate, butyl polymethacrylate, poly(methyl acrylate), Acrylic derivative system polymer, such as ethyl polyacrylate, polyacrylic acid, polymethacrylic acid, and polyacrylamide; Polyvinyl fluoride, Fluororesin, such as polyvinylidene fluoride and polytetrafluoroethylene; Polyacrylonitrile, CN basis content polymer, such as a polyvinylidenecyanide; conductive polymers, such as containing halogen polymer; poly aniline, such as polyvinyl alcohol system polymer; polyvinyl chloride, such as polyvinyl acetate and polyvinyl alcohol, and a polyvinylidene chloride, etc. can be used. It can be used even if it is mixtures, such as the above-mentioned polymer, a conversion object, a derivative, a random copolymer, an alternating copolymer, a graft copolymer, a block copolymer, etc. The molecular weight of these resin is 100000–1 million preferably [ it is desirable and ] to 10000–3 million and a pan. If too low, the intensity of an active material layer will fall, and when too high, it is in the tendency for viscosity to become high and for formation of an electrode to become difficult.

[0055]As loadings of the binder to 100 copies of active materials, 0.1 to 30 copies are one to 20 copies still more preferably preferably. When there is too little quantity of a binder, the intensity of an electrode may fall, and when too large, it is in the tendency for ionic conductivity to fall. In an active material layer, a granular material, a filler, etc. which reveal various kinds of functions, such as an electrical conducting material and a reinforcing member, if needed may be contained. If it mixes to the above-mentioned active material in proper quantity and conductivity can be given to it as an electrical conducting material, there will be no restriction in particular, but the end of carbon powder, such as acetylene black, carbon black, and black lead, the fiber of various kinds of metal, foil, etc. are usually mentioned. The DBP oil absorption of a conductive substance is preferred in not less than 120cc/100 g, and preferred in the end of carbon powder from the reason for holding an electrolysis solution in not less than 150cc/100 g especially. As a reinforcing member, various kinds of inorganic and organic globular shapes, a fibrous filler, etc. can be used.

[0056]An electrode can be manufactured by applying and drying the paint containing the material which constitutes an active material layer on a charge collector. Consolidation processing can also be presented with an active material layer after that. The volume fraction of the binder in an active material layer is controllable by controlling the presentation of a paint, a drying condition, a consolidation condition, etc. Since the adhesive property between an active material layer and a charge collector is raised if needed, an undercoat primer layer can be provided among these.

[0057]When using an undercoat primer layer, the resin which added conductive particles, such as carbon black, graphite, and metal powder, as the presentation, and conductive organic conjugated system resin can be illustrated. It is good to use preferably the carbon black which may function on a conductive particle also as an active material, and graphite. When poly aniline, polypyrrole, poly acene, a disulfide system compound, a polysulfide system compound, etc. which may function as active materials also as resin are used, it is desirable in order not to decrease capacity. As for the rate of resin over a conductive particle, in the presentation which uses as the main ingredients the resin which added the conductive particle, it is preferred to consider it as 1 to 300 % of the weight. When too low, film strength may fall and the exfoliation on a process, etc. may arise at the time of cell use. When too high, it is in the tendency for conductivity to fall and for a battery characteristic to fall. It is preferred to consider it as 5 to 100% of the weight of the range preferably especially.

0.05–10 micrometers of thickness of an undercoat primer layer are usually 0.1–1 micrometer preferably. If too thin, spreading will become difficult and it will become difficult to secure homogeneity. When too thick, the volume capacity of a cell may be spoiled more than needed.

[0058]An electrolyte exists as a constituent of the electrolyte layer between an anode and a negative electrode. An electrolyte usually exists also in the active material of an electrode as an ion migration phase. As an electrolyte, the thing of various kinds of descriptions, such as an electrolysis solution, a solid polymer electrolyte, a gel electrolyte, and an inorganic solid electrolyte, can be used, for example. Generally, if non fluidity electrolytes, such as a solid polymer electrolyte, a gel electrolyte, and an inorganic solid electrolyte, are used, it will become possible to prevent the leakage to electrolytic case outside more effectively. Since it is in the tendency for an electrolyte to leak to case outside easily when what has shape changeability is especially used as a case in this invention, especially the effect that uses a non fluidity electrolyte is remarkable.

[0059]On the other hand, the electrolysis solution which dissolves lithium salt in a nonaqueous solvent has high mobility, and is in the tendency to excel in ion conductivity compared with a non fluidity electrolyte generally. Therefore, it is preferred to use the electrolyte containing an electrolysis solution at the point which raises ion conductivity. The electrolysis solution used as an electrolyte dissolves lithium salt which is usually a supporting electrolyte in a nonaqueous solvent. As a nonaqueous solvent, the solvent of high permittivity is used comparatively suitably. Specifically Cyclic carbonate, such as ethylene carbonate and propylene carbonate. Non-cyclic carbonate, such as dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate. Nitril, such as sulfur compounds, such as lactone, such as ether, such as a tetrahydrofuran, 2-methyltetrahydrofuran, dimethoxyethane, and diphenyl ether, and gamma-butyrolactone, and sulfolane, and acetonitrile, can be mentioned. They are cyclic carbonate and/or lactone preferably on battery characteristics, such as a cycle characteristic, a rate characteristic, and safety.

[0060]In this invention, the boiling point in ordinary pressure uses a not less than 150 \*\* nonaqueous solvent (it may be called the following "high boiling point solvent") preferably as a solvent of an electrolysis solution. Here, in addition, "the boiling point is not less than X \*\*" means that steam pressure does not exceed 1atm even if it heats from a room temperature to X \*\* under pressure 1atm. That is, when it heats from a room temperature to 150 \*\* under pressure 1atm, it is preferred that steam pressure always uses the nonaqueous solvent which is 1 or less atm. As a result, the higher cycle characteristic has been acquired enough and the safety of a cell can be raised. For example, when the low-boiling point solvent which consists of solvents, such as dimethyl carbonate, diethyl carbonate, and dimethoxyethane, is used, It is generated by air bubbles between an active material and a solvent by evaporation of a solvent, the impregnation states of an electrolysis solution fall, and the heterogeneity of an interface arises, and it is in the tendency for a cycle characteristic to fall easily. Even if it stores a battery element in a shape changeability case by using a high boiling point solvent, the shape change (modification) of the cell in the bottom of an elevated temperature, etc., volatilization of an electrolysis solution, disclosure, etc. can also be controlled. As such a high boiling point solvent, propylene carbonate, ethylene carbonate, butylene carbonate, gamma-butyrolactone, etc. can be mentioned.

[0061]As for a nonaqueous solvent, it is preferred that viscosity is 1 or more mPa-s. As lithium salt which is a supporting electrolyte used for an electrolyte,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiI}$ ,  $\text{LiBr}$ ,  $\text{LiCl}$ ,  $\text{LiAlCl}_4$ ,  $\text{LiHF}_2$ ,  $\text{LiSCN}$ ,  $\text{LiSO}_3\text{CF}_2$ , etc. can be mentioned. Especially among these,  $\text{LiPF}_6$  and  $\text{LiClO}_4$  are preferred. The content in the electrolysis solution of these supporting electrolytes is usually 0.5 – 2.5 mol/l.

[0062]A gel electrolyte can consist of an above-mentioned electrolysis solution and polymer for gel formation. A gel electrolyte usually holds the above-mentioned electrolysis solution by polymer. a gel electrolyte gives ion conductivity comparable as an electrolysis solution -- since things can be carried out and immobilizing of the electrolyte is carried out, in this invention, it is an especially

desirable electrolyte. Although the concentration to the electrolysis solution of polymer in a gel electrolyte is based also on the molecular weight of the polymer to be used, it is usually 0.1 to 30 % of the weight. If concentration is too low, it will become difficult to form gel, and the holdout of an electrolysis solution may fall, and the problem of a flow and liquid leakage may arise. If concentration is too high, while viscosity will become high too much and will produce process top difficulty, it is in the tendency for the rate of an electrolysis solution to fall, for ionic conductivity to fall, and for battery characteristics, such as a rate characteristic, to fall. As polymer to hold, an electrolyte Poly (meta) acrylate system polymers, Various kinds of polymer which has a function which can gel an electrolysis solution, such as alkylene oxide system polymers which have an alkylene oxide unit, polyvinylidene fluoride, fluorine system polymers like a fluoridation vinylidene-hexafluoropropylene copolymer, can be mentioned.

[0063]Material and processes as occasion demands, such as the method of carrying out immobilizing processing of the electrolyte paint which dissolved polymer in the electrolysis solution beforehand as a method of forming a gel electrolyte, and the method of making carry out crosslinking reaction of the electrolyte paint which made the electrolysis solution contain a polymerization nature gelling agent, and using as a non fluidity electrolyte, are employable. In performing the paint which made the electrolysis solution contain a polymerization nature gelling agent for formation of a gel electrolyte by the method of carrying out crosslinking reaction, it prepares a paint by performing polymerization, such as ultraviolet curing and heat curing, by adding to an electrolysis solution by making into a polymerization nature gelling agent the ingredient used as the monomer which forms polymers.

[0064]As a polymerization nature gelling agent, what has unsaturated double bonds, such as an acrylyl group, a methacryloyl group, a vinyl group, and an allyl group, for example is mentioned. Specifically, for example Acrylic acid, methyl acrylate, ethyl acrylate, Ethoxyethyl acrylate, methoxy ethyl acrylate, ethoxyethoxyethyl acrylate, Polyethylene-glycol monoacrylate, ethoxyethyl methacrylate, Methoxy ethyl methacrylate, ethoxyethoxyethyl methacrylate, Polyethylene-glycol-monomethacrylate, N, and N-diethylamino ethyl acrylate, N and N-dimethylamino ethyl acrylate, glycidyl acrylate, Allyl acrylate, acrylonitrile, N-vinyl pyrrolidone, diethylene glycol diacrylate, Triethylene glycol diacrylate, tetraethylene glycol diacrylate, Polyethylene-glycol diacrylate, diethylene-glycol dimethacrylate, Triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, Polyethylene glycol dimethacrylate, polyalkylene glycol diacrylate, polyalkylene glycol dimethacrylate, trimethylolpropanalkoxy RETOTORI acrylate, These which can illustrate pentaerythritol alkoxy RETOTORI acrylate, pentaerythritol alkoxylate tetraacrylate, ditrimethylol propane alkoxylate tetraacrylate, etc. can use two or more sorts together. diacrylate and doria which contain two or more ethylene oxide groups preferably especially in these -- it is KURIRETO. Although the content in particular of the polymerization nature gelling agent in an electrolysis solution is not restricted, it is 1 % of the weight or more preferably. If content is low, the formation efficiency of polymers will fall and it will become difficult to carry out immobilizing of the electrolysis solution. On the other hand, since remains of an unreacted monomer and the operativity as an electrolyte paint will worsen if too large, it may usually be 30 or less % of the weight.

[0065]When making it form by the method of carrying out immobilizing of the electrolyte paint which contained polymer for the gel electrolyte beforehand, it is preferred to use as polymer the polymers which dissolve in an electrolysis solution at an elevated temperature, and form a gel electrolyte at ordinary temperature. That is, it is considered as a gel electrolyte by making into ordinary temperature the polymer which dissolved in the electrolysis solution at the elevated temperature. As a temperature at the time of an elevated temperature, 50-200 \*\* is usually 100-160 \*\* preferably. The stability of a gel electrolyte falls that it seems that it dissolves at low temperature too much. If a melting temperature is too high, decomposition of an electrolyte component, polymer, etc. can be caused. Forced cooling can also be carried out although it is preferred as the method of immobilizing to allow an electrolysis solution to stand at a room temperature. Polymer which has rings, such as polyvinyl pyridine and Polly N-vinyl pyrrolidone, as polymer which can be used, for

example; Poly methyl methacrylate, Ethyl polymethacrylate, butyl polymethacrylate, poly(methyl acrylate), Acrylic derivative system polymer, such as ethyl polyacrylate, polyacrylic acid, polymethacrylic acid, and polyacrylamide; Polyvinyl fluoride, Fluororesin, such as polyvinylidene fluoride; CN basis content polymer; polyvinyl acetate, such as polyacrylonitrile and a polyvinylidenecyanide, Polyvinyl alcohol system polymer, such as polyvinyl alcohol; containing halogen polymer, such as polyvinyl chloride and a polyvinylidene chloride, etc. are mentioned. Poly methyl methacrylate, polyacrylonitrile, polyethylene oxide, or those denaturation objects are preferably used in these. The mixture of the above-mentioned polymer, a conversion object, a derivative, a random copolymer, an alternating copolymer, a graft copolymer, a block copolymer, etc. can also be used.

[0066]The ranges of the weight average molecular weight of these polymer are 10,000–5,000,000 preferably. If a molecular weight is low, it will become difficult to form gel, and if another side and a remainder molecular weight are high, viscosity will become high too much and handling will become difficult. In the method of forming these gel electrolytes, since the method of making carry out crosslinking reaction of the electrolyte paint which made the electrolysis solution contain a polymerization nature gelling agent, and using as a non fluidity electrolyte becomes inter-electrode adhesion improves and especially remarkable [ the effect of this invention ], it is desirable.

[0067]In an electrolyte, various kinds of additive agents can be added if needed for the improved efficiency of a cell. As an additive agent which makes such a function reveal, Although limitation in particular is not carried out, trifluoro propylene carbonate, 1,6-dioxo spiro[4,4] nonane- 2,7-dione, 12-crown 4-ether, vinylene carbonate, catechol carbonate, a succinic anhydride, etc. are mentioned.

[0068]An electrolyte layer makes an electrolyte usually come to be impregnated into the spacer which consists of porous sheets. A spacer is the porous film provided between the anode and the negative electrode, isolates these and it supports an electrolyte layer. As a material of a spacer, polymers, such as polyolefines, such as polyethylene and polypropylene, polyolefines by which some or all of these hydrogen atoms was replaced with the fluorine atom, polyacrylonitrile, and polyaramide, can be mentioned. Preferably, they are polyolefine and the polyolefines by which fluoride substitution was carried out. Specifically, polyethylene, polypropylene, PORITETO truck fluoroethylene, polyvinylidene fluoride, etc. can be mentioned. Of course, they may be a copolymer containing the monomer unit of the above-mentioned polymer, and a mixture of polymer. A spacer may be the oriented film formed by 1 axis extension and biaxial extension, and may be a nonwoven fabric. 100 micrometers or less of thickness [ 50 micrometers or less of / 30 micrometers or less of ] of a spacer are usually 20 micrometers or less most preferably still more preferably. When thickness is too large, it is in the tendency for the rate characteristic and volume energy density of a cell to fall. Since cutting tends to become difficult by rigidity insufficiency and it is easy to produce a short circuit when too thin, not less than 7 micrometers is not less than 5 micrometers usually not less than 8 micrometers still more preferably preferably. The voidage of a spacer is usually 45–75% preferably 45 to 90%. If voidage is too large, mechanical strengths run short, and when too small, it is in the tendency for the rate characteristic of a cell, etc. to fall.

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[Translation done.]

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EXAMPLE

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[Example]Hereafter, although this invention is explained still in detail based on an example, this invention is not limited at all by the following example, in the range which does not change the gist, can be changed suitably and can be carried out. It shows a weight section that it is especially with a "part" in the following explanation, unless it refuses.

90 copies of example of anode manufacture 1 cobalt acid lithium, five copies of acetylene black, five copies of polyvinylidene fluorides, and 80 copies of N-methyl-2-pyrrolidone were kneaded with the kneading machine for 2 hours, and it was considered as the anode paint 1.

[0070]Next, the anode paint 1 was applied by die coating of the extrusion die on the aluminum collector substrate of 20-micrometer thickness, it dried, and the active material layer which consists of a porous membrane with which the active material was bound on the charge collector with the binder was made to form. Subsequently, using the roll press (calendar), after consolidation, it cut and was considered as the anode 1.

90 copies of example graphite of negative-electrode manufacture (particle diameter of 15 micrometers), ten copies of polyvinylidene fluorides, and 100 copies of N-methyl-2-pyrrolidone were kneaded with the kneading machine for 2 hours, and were made into the negative-electrode paint 1.

[0071]Next, the negative-electrode paint 1 was applied by die coating of the extrusion die on the copper charge collector substrate of 20-micrometer thickness, it dried, and the active material layer which consists of a porous membrane with which the active material was bound on the charge collector with the binder was made to form. Subsequently, using the roll press (calendar), after consolidation, it cut and was considered as the negative electrode 1.

Ethylene carbonate containing  $\text{LiPF}_6$  of example of electrolyte paint creation 11 M concentration, Propylene carbonate and 925 copies of mixed liquor of phenyl ether (ethylene carbonate: volume ratio; propylene carbonate : phenyl ether =7.3:7.3:1), 44 copies of tetraethylene glucol diacrylate, and polyethylene oxide -- doria -- the mixed stirring dissolution of 22 copies of KURIRETO, two copies of polymerization initiators, and nine copies of additive agents (succinic anhydride) was carried out, and it was considered as the electrolyte paint 1.

Apply the electrolyte paint 1 to the example 1 anode 1 and the negative electrode 1, and after laminating on both sides of the porosity film made from polyethylene independently dipped in the electrolyte paint 1 in between, immobilizing of the electrolyte is carried out by heating at 90 \*\* for 10 minutes, An anode and a negative electrode as shown in drawing 9, and the plate-like unit battery element which has an immobilizing nature electrolyte were created.

[0072]The terminal area of anodes and negative electrodes was bundled after laminating the obtained unit battery element, and the lead which takes out current to each terminal area was connected. Then, the laminate film with a thickness of about 100 micrometers which has a resin layer to both sides of an aluminum layer was accommodated in a sheathing material like drawing 9 which carried out opposite shaping. Then, the joining piece part (equivalent to the joining piece part 4A in drawing 5) except the neighborhood which took out the lead for the laminate film after



enclosure with the vacuum seal was bent so that an entire-covering part might be met. The cell capacity of the flat cell A created in this way was 650mAh.

[0073]In the flat cell A created as mentioned above, it is 3 cycle \*\*\*\*\* about the charge and discharge between nominal working voltage at the constant current of 0.65A. This cell was inserted into assembling-die metal member holding like drawing 22 which adjusted opening height with the screw to 110% of the total thickness of the cell, and the overcharge examination was done. Upper limit voltage is set as 10V, and that is, charging a cell by the constant current of 1.8C (1.17A) from a discharge state was continued for 200 minutes. The thickness of the cell of a discharge state was 3.9 mm (the thickness of an electrode is 3.7 mm). Disclosure of the gas at the time of overcharge was not observed at all, but the maximum temperature of the battery surface was 94 \*\*. It was a grade in which most bulging of the cell by gas is not observed by the cell after overcharge, but a cell loosens slightly. The thickness of the cell after overcharge was 4.2 mm (the thickness of an electrode is 4.0 mm). Even if such a cell applied the pressure to the cell after overcharge, disclosure of the gas by the tear of a sheathing material was not observed.

[0074]As a result of inserting the flat cell A into member holding by the same method as the above, setting upper limit voltage as 10V and continuing charging a cell for 120 minutes by the constant current of 1.95A from a discharge state, disclosure of the gas at the time of overcharge was not observed at all, but the maximum temperature of the battery surface was 132 \*\*. It was a grade in which most bulging of the cell by gas is not observed by the cell after overcharge, but a cell loosens slightly. The thickness of the cell after overcharge was 4.3 mm (the thickness of an electrode is 3.8 mm). Even if such a cell applied the pressure to the cell after overcharge, disclosure of the gas by the tear of a sheathing material was not observed.

a reference example -- the flat cell A (15 cm of monotonous each one product <sup>2)</sup> created as mentioned above -- the constant current of 0.65A -- the charge and discharge between nominal working voltage -- 3 cycle \*\*\*\*\*. The thickness of the cell of a discharge state was 3.9 mm (the thickness of an electrode is 3.7 mm). Next, upper limit voltage being set as 10V, and charging a cell by the constant current of 1.8C (1.17A) from a discharge state by the method to which load is applied according to bulging of a cell was continued for 200 minutes. As a result, bulging of the cell by gas was not observed at all by the cell after overcharge, but the thickness of the cell after overcharge was 4.6 mm (the thickness of an electrode is 4.3 mm). Under the present circumstances, the maximum load applied to the cell was 8.3 kg ( $8.3/15=0.55 \text{ kg/cm}^2$ ). The maximum temperature of the battery surface in this case was 85 \*\*.

The overcharge examination of the cell A was done on comparative example 1 member holding like Example 1 except not having accommodated the flat cell A.

[0075]As a result, the cell blistered during overcharge, it fumed 72 minutes afterward, and disclosure of the gas at the time of overcharge was observed. The maximum temperature of the battery surface in that case was 140 \*\*. Upper limit voltage was set as 10V on the same conditions, and as a result of continuing charging a cell by the constant current of 1.95A from a discharge state, the cell ignited 38 minutes afterward. From a reference example, by applying the pressure of specification (more than  $0.5 \text{ kg/cm}^2$ ) on a cell at the time of overcharge shows that the safety of the cell at the time of overcharge can be improved. That is, if member holding is designed so that the power which is equivalent to this load at the time of overcharge may be added, it turns out that the safety at the time of overcharge improves. If Example 1 is compared with the comparative example 1, the safety at the time of overcharge will actually improve by storing a cell to member holding so that a pressure may be added at the time of overcharge.

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[Translation done.]



\* NOTICES \*

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1]It is an exploded perspective view of the cell concerning an embodiment.

[Drawing 2]It is a sectional view of the important section of the cell concerning an embodiment.

[Drawing 3]It is a perspective view showing the battery element of the cell concerning an embodiment.

[Drawing 4]It is a perspective view (before adherence of a joining piece part) of the cell concerning an embodiment.

[Drawing 5]It is a perspective view (after adherence of a joining piece part) of the cell concerning an embodiment.

[Drawing 6]It is a sectional view of the case concerning an embodiment.

[Drawing 7]It is a typical sectional view showing signs that a cell blisters.

[Drawing 8]It is a sectional view of the case concerning another embodiment.

[Drawing 9]It is a perspective view in the middle of manufacture of the cell concerning another embodiment.

[Drawing 10]It is a perspective view in the middle of manufacture of the cell concerning another embodiment.

[Drawing 11]It is a perspective view in the middle of manufacture of the cell concerning an embodiment different furthermore.

[Drawing 12]It is a top view in the middle of manufacture of drawing 11.

[Drawing 13](A) and the (B) figure are drawings of longitudinal section showing an example of the composite which constitutes a sheathing material, respectively.

[Drawing 14]It is drawing of longitudinal section showing other examples of the composite which constitutes a sheathing material.

[Drawing 15]It is a typical sectional view of an example of a unit battery element.

[Drawing 16]It is an expanded sectional view of the tab portion of a battery element.

[Drawing 17]It is a perspective view of the cell concerning another embodiment.

[Drawing 18]It is a typical exploded perspective view of the member holding concerning one embodiment of this invention.

[Drawing 19]A battery element is an A-A arrowed cross-section figure of drawing 18 showing signs that it was stored by member holding.

[Drawing 20]It is a typical exploded perspective view of the member holding concerning another embodiment of this invention.

[Drawing 21]It is a typical exploded perspective view of the member holding concerning another embodiment of this invention.

[Drawing 22]It is a typical exploded perspective view of the member holding concerning another embodiment of this invention.

[Description of Notations]

1 Battery element  
2, 3, 6, 7, and 8 Sheathing material  
4a and 4b Tab  
4A, 4F, and 4G Joining piece part  
4B Entire-covering part  
5 Insulating material  
11 Anode  
11a Positive active material  
12 Negative electrode  
12b Negative electrode active material  
13 Non fluidity electrolyte layer  
15a Positive pole collector  
15b Negative pole collector  
21 Lead  
22 Positive pole collector  
23 Positive active material  
24 Spacer (electrolyte layer)  
25 Negative electrode active material  
26 Negative pole collector  
40 Metal layer  
41 and 42 Synthetic resin layer  
43 Adhesives layer  
181 Member holding

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[Translation done.]

\* NOTICES \*

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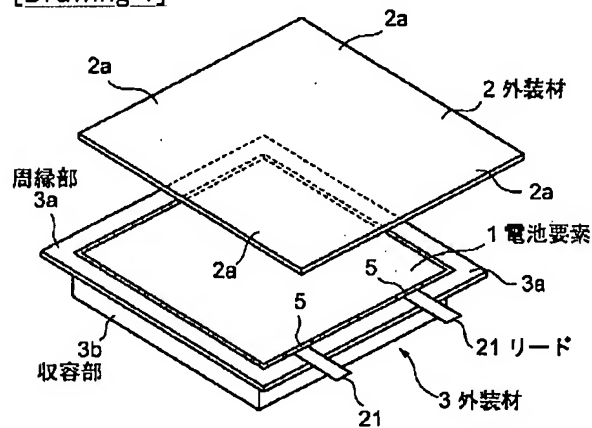
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2.\*\*\*\* shows the word which can not be translated.

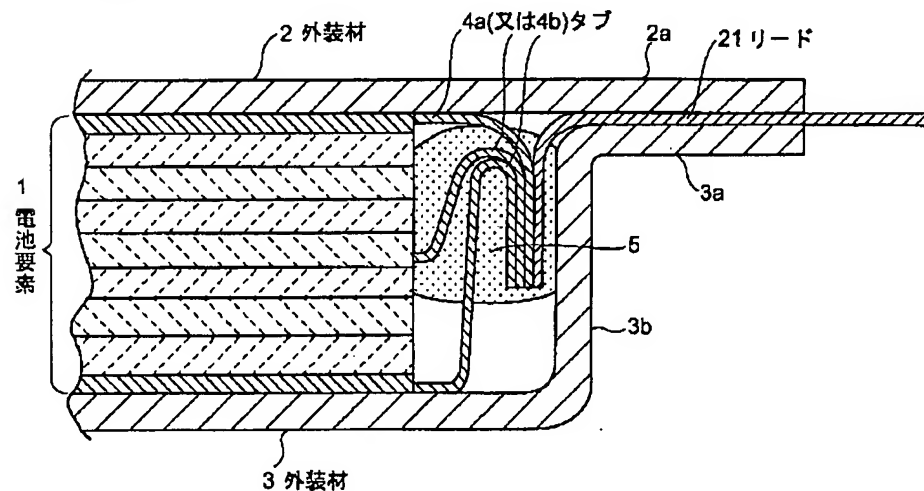
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## DRAWINGS

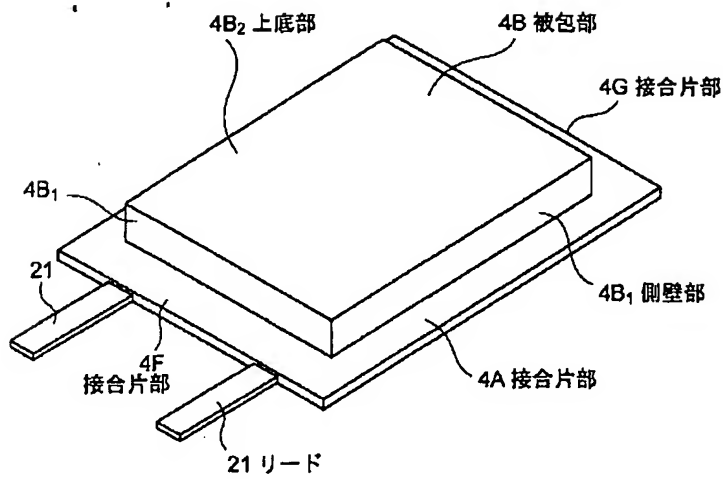
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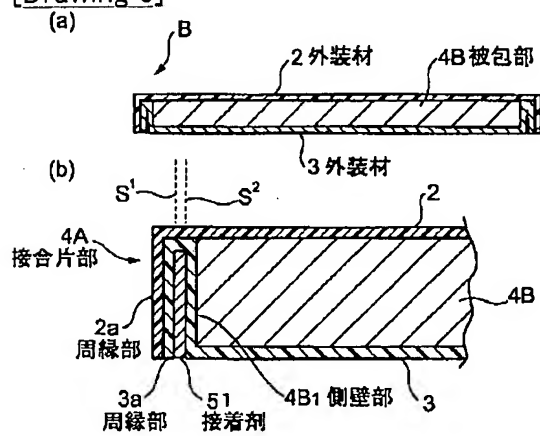
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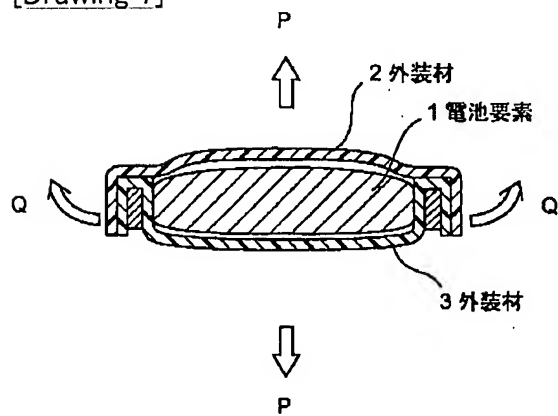
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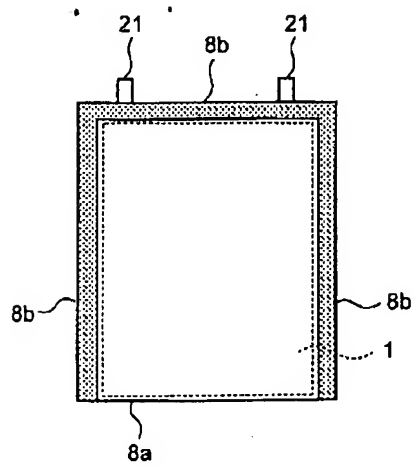
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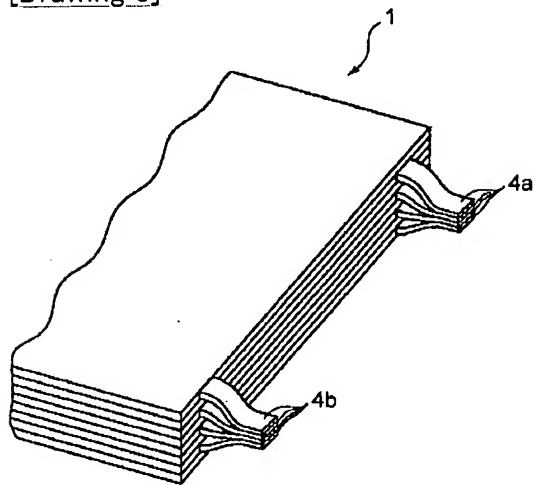
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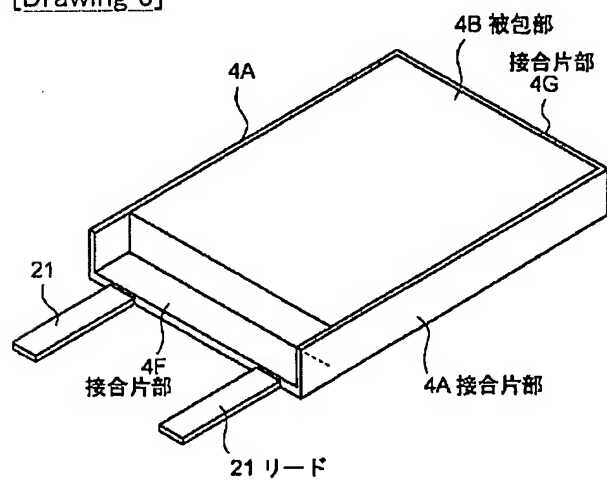
[Drawing 12]



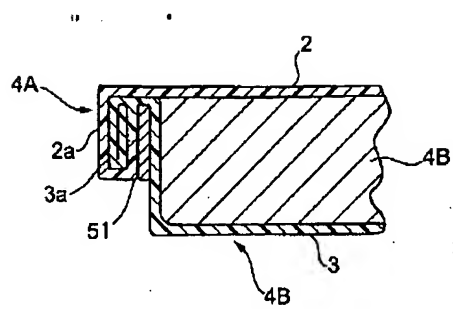
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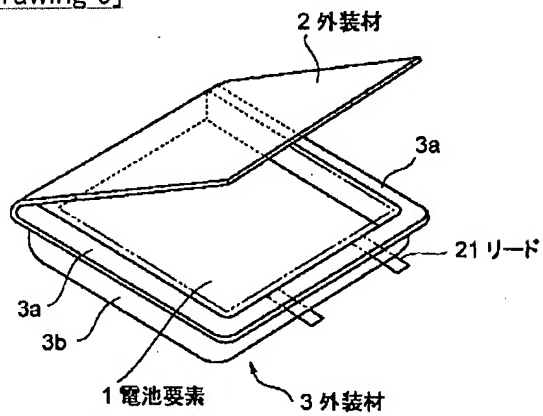
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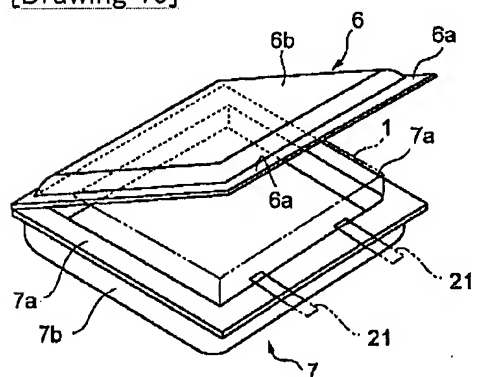
[Drawing 8]



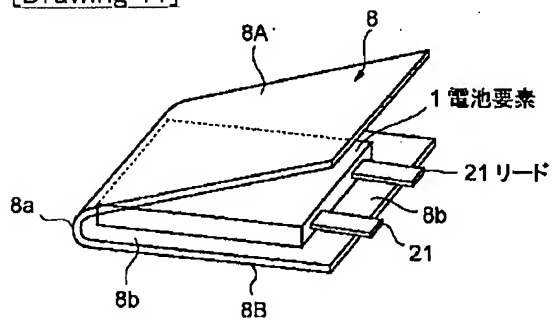
[Drawing 9]



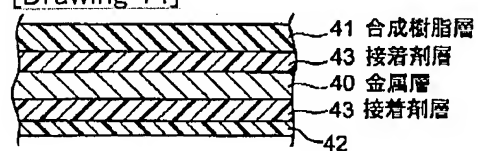
[Drawing 10]



[Drawing 11]



[Drawing 14]

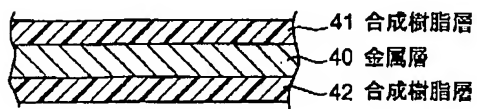


[Drawing 13]

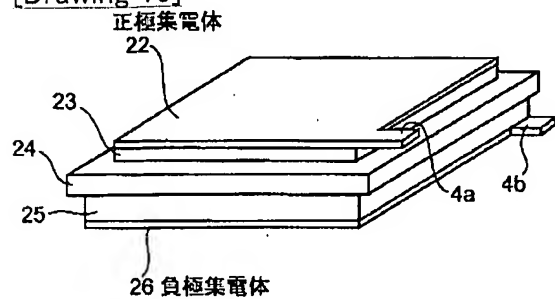
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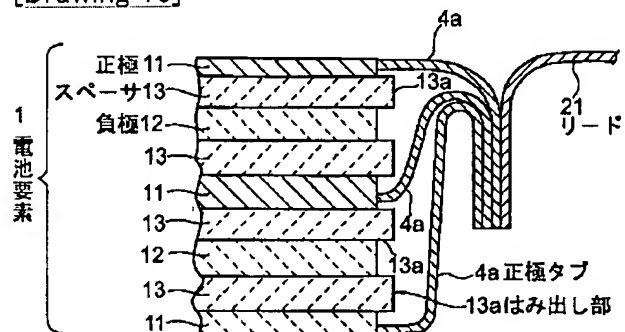
(B)



[Drawing 15]

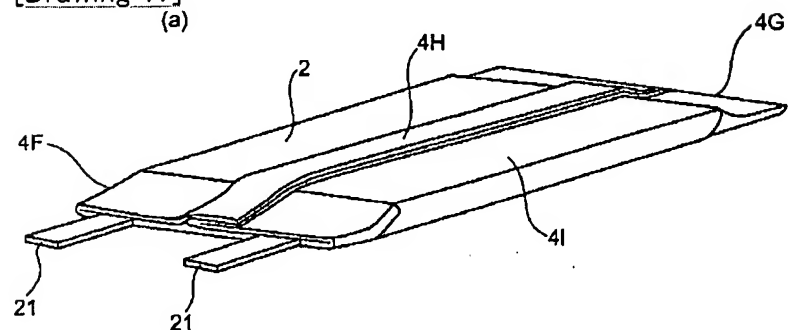


[Drawing 16]



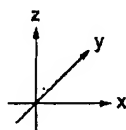
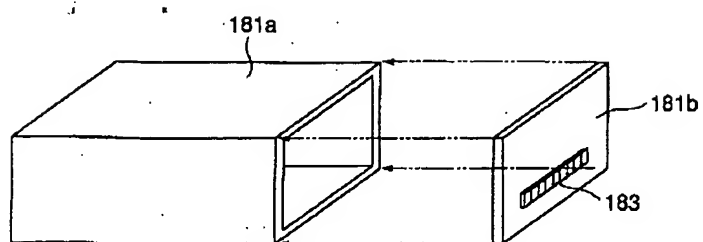
[Drawing 17]

(a)

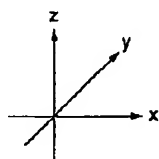
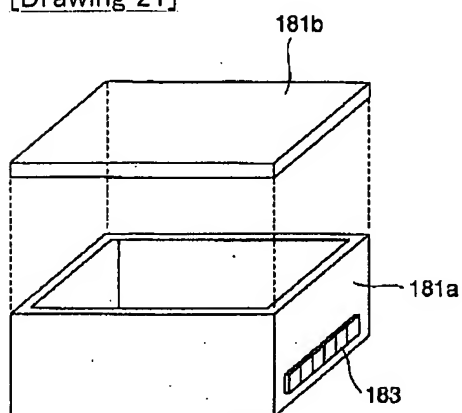


[Drawing 20]

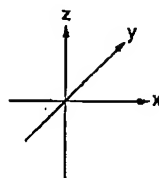
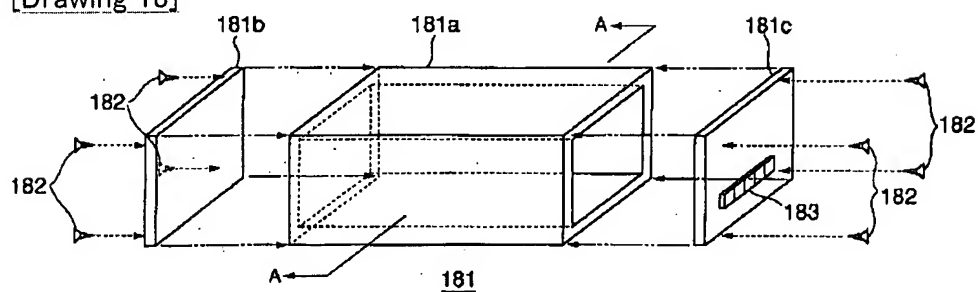




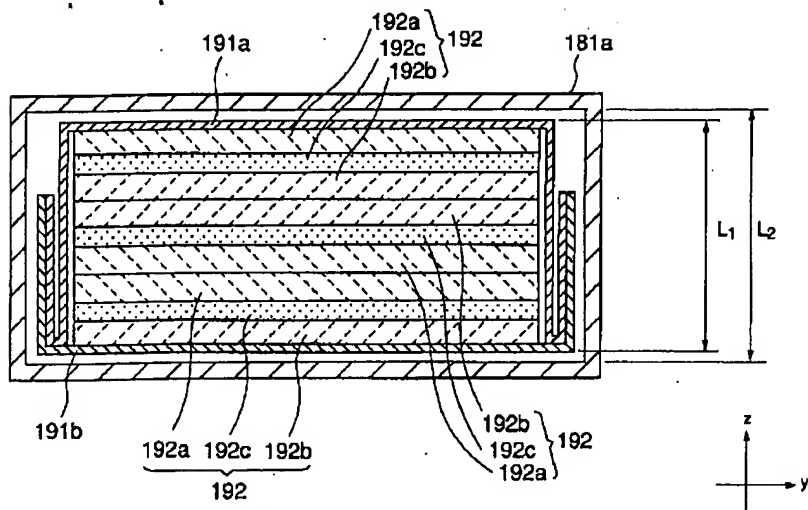
[Drawing 21]



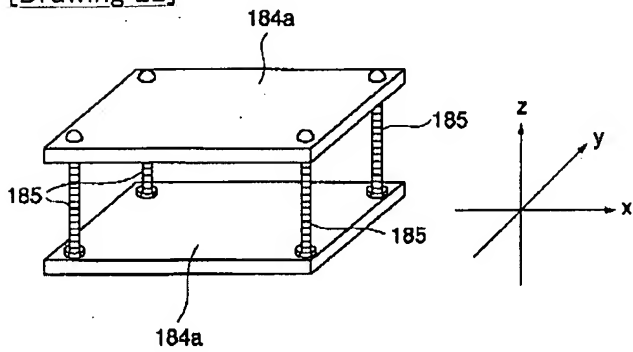
[Drawing 18]



[Drawing 19]



[Drawing 22]



[Translation done.]

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : MITSUBISHI CHEMICALS CORP

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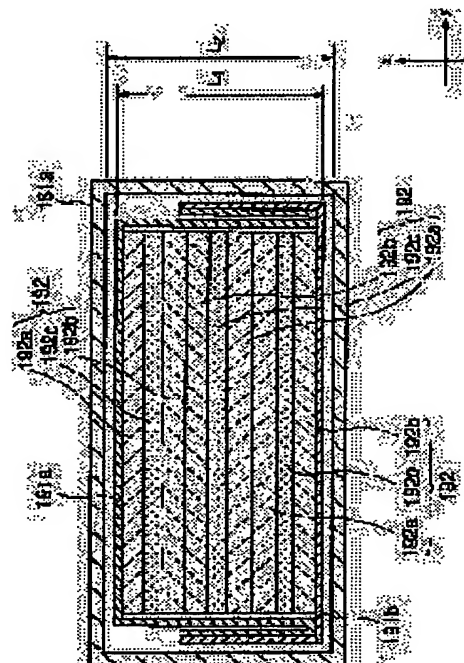
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KAWAI TOMOHIRO

**(54) ACCOMMODATION MEMBER FOR LITHIUM SECONDARY BATTERY AND SECONDARY BATTERY PACK USING IT**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To enhance a safety at the time of excess charging.**SOLUTION:** When the lithium secondary battery in which a battery element having a positive electrode and a negative electrode is accommodated in a flat plate-like case comprising an outer packaging material is accommodated in an accommodation member, a vertical strength of the accommodation member against a flat plate surface of the case is made to a strength withstanding a pressure of 0.5 kg/cm<sup>2</sup> or more.

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10/40		10/40	Z 5 H 0 2 9
H 0 2 J 7/00	3 0 1	H 0 2 J 7/00	3 0 1 B 5 H 0 4 0

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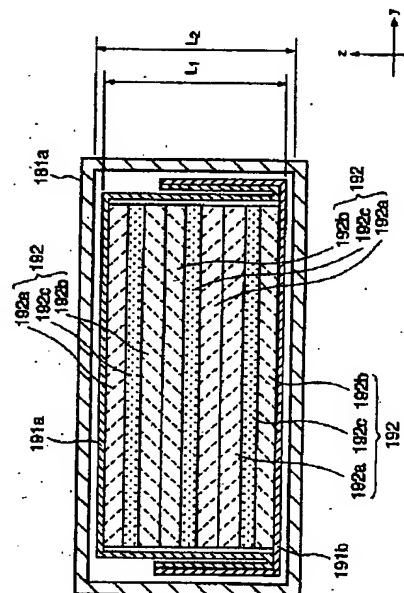
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(54) 【発明の名称】 リチウム二次電池用収容部材及びそれを用いた二次電池パック

(57) 【要約】

【目的】 過充電時の安全性を向上させる。

【解決手段】 正極及び負極を有する電池要素が外装材からなる平板状ケースに収納されてなるリチウム二次電池を収容部材に収納する際に、上記ケースの平板面に対して垂直方向の収容部材強度を0.5 kg/cm<sup>2</sup>以上の圧力に耐えうる強度とする。



## 【特許請求の範囲】

【請求項1】 正極、負極及び電解質を有する電池要素が外装材からなる平板状ケースに収納されてなるリチウム二次電池を収容する収容部材において、上記ケースの平板面に対して垂直方向の強度が $0.5\text{ kg/cm}^2$ 以上の圧力に耐えうる強度であることを特徴とするリチウム二次電池用収容部材。

【請求項2】 収容部材の収容部の高さが、リチウム二次電池の総厚さの101~120%である請求項1に記載のリチウム二次電池用収容部材。

【請求項3】 請求項1又は2に記載の収容部材内部に、正極、負極及び電解質を有する電池要素が外装材からなる平板状ケースに収納されてなるリチウム二次電池を収容してなる二次電池パック。

【請求項4】 外装材の厚みが0.2mm以下である請求項3に記載の二次電池パック。

【請求項5】 リチウム二次電池の厚みが2mm以上である請求項3又は4に記載の二次電池パック。

【請求項6】 電池の公称容量が100mAh以上である請求項3乃至5のいずれか1つに記載の二次電池パック。

【請求項7】 外装材が合成樹脂層とガスバリア層とが積層されたラミネートフィルムよりなる請求項3乃至6のいずれか1つに記載の二次電池パック。

【請求項8】 電池要素が、正極と負極との間に非流動性電解質を有する請求項3乃至7のいずれか1つに記載の二次電池パック。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は二次電池に関し、詳しくは、過充電時の安全性が向上した二次電池に関する。

## 【0002】

【従来の技術】 近年開発されてきている高エネルギー密度のリチウム二次電池は、そのエネルギー密度の高さ故に、電池の誤用や使用機器の故障等による発火、発煙等の危険性が高まっている。このような背景から、二次電池の安全性の確保は、より高エネルギー密度化された現在の電池設計において、必要不可欠な課題の一つとなっている。

【0003】 電池の安全性確保の中では、特に過充電に対する安全性確保が重要な課題の一つである。これは、二次電池を充電する際に何らかの原因で所定以上の電気が流れると電池が過充電状態となり、その結果内部短絡等が起り、電池温度の上昇を伴って電池の発煙、発火等の事故に繋がる危険性が相対的に高いためである。例えば、一般に、リチウム二次電池は、過充電状態になると、まず電解液等の分解によりガスの発生が起る。ガス発生が生じると、電池の破裂、漏液等に繋がるばかりでなく、この状態が続くことによって最終的に電池温度が上昇し、発煙、発火等の事故に繋がることさえもあ

る。そのような観点から、これまでに過充電に対する種々の防止方法が提案されてきた。

## 【0004】

【発明が解決しようとする課題】 過充電防止策の具体的方法としては、電池外部に付属させた電子回路による制御方法、過充電時の電解液等の分解によって発生するガスを利用した安全弁による機械的電流遮断方法等が一般的な方法として知られている。しかしながら、このような方法においては、電池に電子回路や安全弁を搭載する必要上、電池コストが上昇したり、また電池の設計上の制約が生じたりするといった問題点があった。

【0005】 近年においては、ガスバリア層の両面に樹脂層を設けてなるラミネートフィルムのような軽量の外装材を用いて平板状ケースを構成し、この中に正極及び負極を有する電池要素を密閉するタイプの電池が開発されている。このような電池は、外装材として軽量のフィルムを用いることができるので、従来の金属からなるケースに比べていくつかわり点がある。即ち、電池をより軽量・小型化できるだけでなく、電子回路や安全弁を含む金属部からなるケースを用いた場合に比べてケースの構成がより単純なので、コスト的にも有利になることも期待される。一方、このような電池においては、前述の電子回路による制御方法や安全弁による機械的電流遮断方法は、電池ケースの構成上特に困難であるという問題がある。

【0006】 一方、過充電防止策の具体的方法としては、電池の温度上昇によるセパレータの融解を利用したシャットダウンによる方法や、過充電時の正極電位より貴な電位に酸化電位を有する過充電防止剤を電解液に添加することにより、過充電状態で正極電位が上昇した際に有機添加剤の酸化反応を引き起こして過充電時の電池内暴走反応を抑制する方法も知られている。しかしながら、前者のセパレータによるシャットダウン方法は、過充電時の暴走反応が急激であるため、過充電保護として十分に機能させるのが困難なことがある。また、後者の方法においては、電池の充放電に直接関与するわけではない過充電防止剤を電解液に添加するために電池性能に悪影響を与えたり、或いは過充電時の過充電防止剤の酸化反応の結果ガスが発生し、この発生ガスによる使用機器の腐食や有機ガス等の有毒ガスの漏洩等が懸念される。

## 【0007】

【課題を解決するための手段】 本発明者らは、上記目的を達成すべく鋭意検討を重ねた結果、過充電時の電池内でのガスの発生は、過充電時に電極間にある特定以上の圧迫が加わると抑制できること、及び、過充電時の電池のガスの発生を抑制すると、電池の膨れによる使用機器の破損ならびに電池からの腐食性ガス、有毒性ガスの漏洩を防止できるばかりでなく電池温度の上昇も抑制できる為、電池の発煙、発火への危険性をさらに減らすこと

ができることを見出し、本発明を完成した。

【0008】即ち、本発明の要旨は、下記に存する。

(1) 正極、負極及び電解質を有する電池要素が外装材からなる平板状ケースに収納されてなるリチウム二次電池を収容する収容部材において、上記ケースの平板面に対して垂直方向の強度が $0.5\text{ kg/cm}^2$ 以上の圧力に耐えうる強度であることを特徴とするリチウム二次電池用収容部材。

(2) 収容部材の収容部の高さが、リチウム二次電池の総厚さの101～120%である(1)のリチウム二次電池用収容部材。

(3) (1)又は(2)の収容部材内部に、正極、負極及び電解質を有する電池要素が外装材からなる平板状ケースに収納されてなるリチウム二次電池を収容してなる二次電池パック。

(4) 外装材の厚みが $0.2\text{ mm}$ 以下である(3)に記載の二次電池パック。

(5) リチウム二次電池の厚みが $2\text{ mm}$ 以上である

(3)～(4)の二次電池パック。

(6) 電池の公称容量が $100\text{ mAh}$ 以上である(3)～(5)の二次電池パック。

(7) 外装材が合成樹脂層とガスバリア層とが積層されたラミネートフィルムよりなる(3)～(6)の二次電池パック。

(8) 電池要素が、正極と負極との間に非流動性電解質を有する(3)～(7)の二次電池パック。

【0009】

【発明の実施の形態】以下、本発明の実施態様につき説明する。図18は、本発明の一実施形態に係る収容部材の模式的な分解斜視図、図19は、電池要素が収容部材に収納された様子を示す、図18のA-A矢視断面図である。なお、図中、xで示す方向を左右方向、yで示す方向を前後方向、zで示す方向を厚さ方向と便宜上表記することができる。

【0010】収容部材181は、筒体181aと、2つの蓋体181b及び181cとからなる。筒体181aは、上面部と下面部と前面部と背面部とを有する無蓋筒状体であり、全体としてxy平面に広がる平板状の直方体形状を有する。筒体181aは、一体成型された樹脂製部材である。また、筒体181aは、図中左右方向に外部に開口する収容部(空間部)を有する。蓋体181b及び181cは、それぞれyz方向に広がる平板形状の樹脂製部材であり、筒体181aの左右の面で筒体181aと固着され、収容部を外周と隔離する。筒体181aと蓋体181b及び181cとは、それぞれ、ねじ182にてねじ止めされる。蓋体181cには、電池要素の正極及び負極と接続された端子部182が設けられる。

【0011】収容部には、電池要素が収納される。電池要素は、正極192aと負極192bとを電解質層(ス

ペーサ)193cを介して積層してなる単位電池要素を上記積層方向に複数(この場合3)積層してなる。電池要素は、全体としてxy方向に広がる平板形状を有する。電池要素は、2枚の外装材191a及び191bからなるケースに真空封止されている。

【0012】本発明においては、xy方向に広がる上記ケースの平板面に対して垂直な方向(図19において厚さ方向z)の前記収容部材181の強度を $0.5\text{ kg/cm}^2$ 以上、好ましくは $0.6\text{ kg/cm}^2$ 以上とする。このような強度の収容部材を用いれば、過充電時に収容部材によって電極を適度な圧力で圧迫することとなり、その結果、過充電時の電池の暴走反応のトリガーとなる電解液の分解反応によるガスの発生量を著しく減少させることができる。この電極間への荷重は、通常の使用条件下では電池の短絡等の弊害に繋がることがあるため、過充電状態時にのみ電極間に圧迫が加わるように収容部材を設計するのが好ましい。即ち、過充電時には、電極の厚みは特に正極からのリチウムイオンの脱ドーブが終了する充電深度付近から顕著に増加する。従って、この現象を利用し、通常の使用時において電極を圧迫しないような収容部材の厚さとし、過充電時に電極が膨れた際には収容部材は電池に密着して膨れを抑える、即ち電池を圧迫するような収容部材の厚さとするのが好ましい。具体的には、通常の使用条件下においても電池を充電すると僅かな電池の膨れがあるのを考慮し、収容部材の収容部の高さ(図19において $L_1$ で示す)を、リチウム二次電池の総厚さ(図19において $L_2$ で示す)の101～120%とするのが好ましい。

【0013】なお、収容部材の上記強度は、あまりに大きいものは現実的に得難いので、通常 $100\text{ kg/cm}^2$ 以下、好ましくは $50\text{ kg/cm}^2$ 以下とする。収容部材の上記強度は、収容部材の材料やその組み付け強度等によって制御できる。上記の例においては、収容部材181は樹脂製のものを用いたが、その材料は特に限定されず、例えば、金属、樹脂と金属とのハイブリッド等各種の材料を用いることができる。また、上記の例においては、筒体181aと蓋体181b及び181cとをねじにて組み付けたが、特に限定されず、例えば、接着剤や接着テープにて留め付けたり、釘にて固定することができる。

【0014】さらに、上記の例においては、収容部材181は、筒体181aと蓋体181b及び181cとからなるものを用いたが、その他、例えば図20に示すように、一方にのみ開口する有底の筒体181aと蓋体181bとからなる収容部材や、図21に示すような、上方(厚さ方向)に開口する有底の筒体181aと蓋体181bとからなる収容部材や、図22に示すような、上下一対の平板状部材184aを複数(この場合4)の脚体185で支持してなる収容部材を用いることができる。これらの場合も、筒体181aと蓋体181bとは、

ねじ、釘、接着剤、接着テープ等で組み付けられる。

【0015】電池要素が収容部材181に収納されてなる二次電池パックは、通常、他の電池使用機器に接続されて使用される。このような電池使用機器としては、携帯電話、携帯端末、携帯用音響機器、コードレスフォニ子機、電池ブックプレーヤー、ページャー、ハンディターミナル、携帯ファックス、携帯コピー、携帯プリンター、ヘッドフォンステレオ、ビデオムービー、液晶テレビ、ハンディークリーナー、ポータブルCD、電機シェーバー、電子翻訳機、自動車電話、トランシーバー、電動工具、電子手帳、電卓、メモリーカード、テーブルコーダー、ラジオ、バックアップ電源、カメラ、ペースメーカーや補聴器等の医療機器等各種の機器を挙げることができる。また、電池パック内に、各種の機能（回路、駆動機器等）を付属させて、電池パック自体を電池使用機器とすることもできる。

【0016】次に、収容部材に収納されるリチウム二次電池について説明する。本発明で使用するリチウム二次電池は、正極及び負極を有する電池要素が外装材からなる平板状ケースに収納されてなるリチウム二次電池全体の厚さがあまりに薄いと過充電時のガスの発生量が相対的に少ないため、1mm以上、特に2mm以上の場合に特に本発明の効果が顕著である。一方、あまりに厚いのは、電池を小型化、軽量化しにくいので、通常5mm以下、好ましくは4.5mm以下、さらに好ましくは4mm以下である。

【0017】また、電池の容量が小さい電池は、過充電時のガスの発生量が相対的に少ないため、公称容量として、通常100mAh以上、好ましくは200mAh以上でのリチウム二次電池を用いる。電池要素は、正極と負極とを有する。電池要素の形状に特に制限はなく、平板状ケースに収納できる各種の形状を採用することができる。例えば、電池要素として、図19に示すような、正極192aと負極192bとを電解質層（スぺーサ）193cを介して積層してなる平板状の単位電池要素を上記積層方向に複数（この場合3）積層してなる平板積層型形状を採用することができる。また、正極と負極とを電解質層を介して積層した帯状の積層体を巻回してなる巻回型形状を採用することもできる。

【0018】以下、正極と負極と非流動性電解質層とを有する平板状の単位電池要素を厚さ方向に複数個積層してなる電池要素を、フィルム状の外装材によって密閉収納されたリチウム二次電池を例として、リチウム二次電池の実施形態につき詳細に説明する。図1は実施の形態に係る電池の分解斜視図、図2はこの電池の要部の断面図、図3は電池要素の概略的な斜視図、図4及び図5は電池の斜視図、図6はケースの断面図（(a)は全体断面図、(b)は(a)のB部分の拡大断面図）、図7は電池が膨れる様子を示す模式的断面図である。なお、説明の便宜上、図1に記載の電池を上下逆向きにして、図

4及び図5に示す。

【0019】この電池は、電池要素1を外装材3の凹部に収容した後、電池要素1の端子部（タブ4a、4b）付近にエポキシ樹脂やアクリル樹脂等の絶縁材料5を注入し、その後外装材2を外装材3に被せ、真空封止により外装材2、3の周縁部2a、3aを接合したものである。図1の通り、外装材2は平板状である。外装材3は方形箱状の凹部よりなる収容部3bと、この収容部3bの4周縁からフランジ状に外方に張り出す周縁部3aとを有した浅い無蓋箱状のものである。

【0020】図3の通り、電池要素1は、複数の単位電池要素を厚さ方向に積層したものである。この単位電池要素からは、タブ4a又は4bが引き出されている。正極からの各タブ4a同士は束ねられて（即ち、相互に重ね合わされ）、正極リード21が接合されて正極端子部が形成されている。負極からのタブ4b同士も束ねられ、負極リード21が接合されて負極端子部が形成されている。

【0021】外装材3の収容部3b内に電池要素1が収容され、絶縁材料5がタブ4a、4b近傍に注入され、正極端子部及び負極端子部近傍の電池要素側面が絶縁材料で被覆された後、外装材2が被せられる。電池要素1から延出した1対のリード21は、それぞれ外装材2、3の1辺部の周縁部2a、3a同士の合わせ面を通して外部に引き出される。その後、減圧（好ましくは真空）雰囲気下で外装材2、3の4周縁の周縁部2a、3a同士が熱圧着、超音波溶着などの手法によって気密に接合され、電池要素1が外装材2、3内に封入される。その後、絶縁材料5は加熱等によって硬化処理に供され、絶縁材料5が端子部近傍で完全に固着する。完全に固着する前に外装材は封止されているので、固着時に電池の形状が変化することはほとんどない。

【0022】周縁部2a、3a同士が接合されることにより、外装材2、3からなるケースが構成される。図4に示すとおり、このケースは、側壁部4B<sub>1</sub>、上底部4B<sub>2</sub>及び下底部（図示せず）によって電池要素1を被包してなる略直方体状の被包部4Bと、前記外装材の周縁部2a、3a同士が接合されてなる接合片部4A、4F、4Gとを有している。

【0023】図4に記載の状態においては、上記接合片部4A、4F、4Gは、電池要素1を被包している被包部4Bの側壁部4B<sub>1</sub>から外方に張り出している。そこで、図5に示すように、これらの接合片部のうち、接合片部4A、4Gを被包部4Bの側壁部4B<sub>1</sub>に沿うように折曲し、接着剤によって被包部4Bの側壁部4B<sub>1</sub>に固着する（固定する）ことができる。即ち、例えば、図6に示すように、接合片部4Aを、被包部4Bの側壁部4B<sub>1</sub>に沿って折曲すると共に、これらを相互に接着剤51によって接着する。接着剤51としては、エポキシ系接着剤、アクリル系接着剤、ウレタン系接着剤、ホッ



トメルト系接着剤、合成ゴム系接着剤等各種のものを使用することができる。無論、複数の接着剤を併用することもできる。接合片部と側壁部との固着強度を制御するために、接着剤の選定に当たっては、接合片部及び側壁部の表面の材質、固着作業時の環境（湿度、温度等）等を考慮する必要があるが、好ましくは、硬化時間が短く、且つ、非水系電池の製造の際に用いられる露点の低い環境下においても容易に硬化するホットメルト系接着剤を使用する。

【0024】このように、接合片部の少なくとも一部（接合片部4A、4G）を側壁部4B<sub>1</sub>に固着することができるが、この際、これら接合片部は所定の固着強度で固着されるのが好ましい。即ち、下記固着強度試験を行なった場合に、前記接合片部が、前記被包部に対して45度以下、好ましくは30度以下、さらに好ましくは20度以下、最も好ましくは10度以下の角度を維持できる程度の強度で固着される。

#### 固着強度試験

電池電圧が3Vにある電池を、上限電圧を10Vとした範囲で、1.8Cの電流で200分間充電し続ける。ただし、1Cは、電池電圧2.7Vから4.2V定電圧で電流値が0になるまで充電して得られた容量を1時間で放電するための電流値である。なお、固着された部分における接合片部と被包部との角度は、接合片部の接着面を含む平面と被包部の接着面を含む平面とのなす角度（図6においては、S1とS2とのなす角度。この場合平行故0度）のことである。

【0025】一般に、過充電状態においては電池は膨れようとする。即ち、過充電時に図7に示すように、電池は方向Pに膨れようとする。本発明においては、この方向Pへの膨れを防ぐように、前記所定の強度の収容部材にて電池要素を収容する。その結果、過充電状態において、より安全な電池を提供することができる。これは、過充電時の初期に発生する膨れを有効に防止することとなり、それ以降の電池の暴走反応を抑制しているものと推定される。

【0026】以上の例においては、接合片部4A、4Gは、側壁部4B<sub>1</sub>に接着剤によって固着されているが、固着の方法は接着剤を使用することに限定されない。例えば、接着テープを用いて接合片部を被包部に固着させることができる。

【0027】また、上記の例においては、接合片部4A、4Gは側壁部4B<sub>1</sub>に沿って1回だけ折曲されているが、例えば、図8に示すように、接合片部4Aを途中でさらにもう一回折曲して、接合片部4Aの先端を接合片部4Aと側壁部4B<sub>1</sub>との間に介在させるようにしてもよい。このように、接合片部を複数回折曲することによって、接合片部の側面から空気等が侵入するのを防止したり、側壁部での機械的強度をさらに向上させたりすることができる。

【0028】図1では、外装材2、3が別体となっているが、本発明では、図9のように外装材2、3が一連一体となっても良い。図9では、外装材3の一辺と外装材2の一辺とが連なり、外装材2が外装材3に対し屈曲可能に連なる蓋状となっている。この外装材2、3が連なる一辺から、収容部3bの凹部が形成されており、この一辺においては接合片部が形成されていない以外は接合片部と同一の構成のものとなる。この図9の場合でも、接合片部4A、4Gは側壁部4B<sub>1</sub>に接着剤によって固着される。

【0029】図1、9では、収容部3bを有した外装材3と平板状の外装材2とが示されているが、本発明では図10のように、それぞれ浅箱状の収容部6b、7bと、該収容部6b、7bの4周縁から張り出す周縁部6a、7aとを有した外装材6、7によって電池要素1を被包してもよい。図10では、外装材6、7が一連体となっているが、前記図1と同様にこれらは別体となってもよい。

【0030】図1、9、10の構成においては、電池要素の収容部が予め形成されているため、電池要素をよりコンパクトに収容でき、また収容自体も容易である。上記の説明においては、電池要素を収容部に収容した後、端子部近傍に絶縁材料が注入されているが、この場合、周縁部の合わせ面や電池要素と外装材との間に絶縁材料が付着・流入して周縁部の接合を阻害したり、設計通りの電池形状にならなったりすることがある。そこで、電池要素の端子部近傍に絶縁材料を供給した後に電池要素を収容部に収容することによって、上記の問題点を回避することができる。特に、図10の場合は、電池要素を収容後に絶縁材料を供給しても電池要素の略上半分には絶縁材料は供給できないので、この製造方法は好ましい。一方、この方法においては、絶縁材料が供給された状態のハンドリングが容易でない電池要素を運搬し、外装材に配置する必要があるので製造時の取り扱いに注意を要する。この点においては前者の方法が好ましいと言える。

【0031】本発明では、図11のように1枚の平たいシート状の外装材8を中央辺8aに沿って2ツ折り状に折り返して第1片8Aと第2片8Bとの2片を形成し、これら第1片8Aと第2片8Bとの間に電池要素1を介在させ、図12の如く、第1片8Aと第2片8Bの周縁部8b同士を接合して電池要素1を封入してもよい。この場合も、接合片部4A、4Gは、電池要素1を被包してなる被包部の側壁部4B<sub>1</sub>に接着剤によって固着される。このように構成された電池にあっても、接合片部を被包部に沿わせて折曲し、さらに接着剤や接着テープで固定しているため、この場合も過充電の初期における電池要素のふくれを有効に防止でき、また電池の側面の強度、剛性が高い。もちろん、折曲された接合片部が被包部から離反することも防止される。また、電池の側面の

強度、剛性が高いので、側面に衝撃を受けた場合でも、活物質に割れが生じることが防止される。

【0032】なお、以上の例においては、接合片部4 A、4 Gは、被包部4 Bの側壁部4 B<sub>1</sub>に固着されているが、側壁部以外の部分に固着させることもできる。例えば、図17に示すように、1枚の外装材2を電池要素の周囲を巻回するようにリード21を引き出した状態で被包すると共に外装材の周縁を接合して、リードを引き出した部分に設けた接合片部4 Fと、その対向辺に設けた接合片部4 Gと、被包部の上面4 Iに沿って設けた接合片部4 Hを形成させた場合、この接合片部4 Hと被包部上面4 Iとを接着剤や接着テープで固着することもできる。

【0033】以上の例においては、また、端子部(タブ4 a、4 b)近傍に絶縁材料5が充填されている。その結果、過充電の初期における電池要素のふくれを有効に防止でき、さらには短絡がより有効に防止される。絶縁材料5としては、合成樹脂が好適であり、エポキシ樹脂、アクリル樹脂、シリコン樹脂などが例示されるが、中でもエポキシ樹脂又はアクリル樹脂が硬化時間が短いので好適である。特に、アクリル樹脂は、電池性能に悪影響を及ぼす可能性が低いので最も好ましい。絶縁材料は、未硬化の流動性のある状態で端子部近傍に供給され、硬化によって完全に端子部近傍で固着する。また、図1においては、絶縁材料5は、正極端子部と負極端子部とのそれぞれ別個に供給されているが、過充電時の安全性をより高めるため、正極端子部から負極端子部に亘る電池要素の側面全体を被覆するのがより好ましい。この端子部近傍の電池要素側面の被覆においては、特に、正極と負極との間にこれらよりも大きいスペースを設け、このスペースのはみ出し部同士を相互に固着するのが好ましい。

【0034】即ち、電池要素にあっては、例えば図16に示されるように、スペース13が正極11及び負極13から若干はみ出させてはみ出し部13 aを形成し、正極11と負極13との短絡を防止している。このはみ出し部13 a同士を絶縁材料で固着することにより、電池要素が積層方向に拘束されるため、過充電時であっても電池要素の膨れが防止され、電池の熱暴走が防止される。無論、絶縁材料は、電池要素の側面全体に亘って供給することができ、また好ましい。

【0035】電池要素を収納する外装材は、形状可変性を有するものが好ましい。その結果、種々の形状の電池を作成しやすいばかりでなく、真空状態で外装材を封止した場合に、電池要素の電極間の貼り合わせを強化する機能を付与することができ、その結果、サイクル特性などの電池特性を向上させることができる。外装材の厚さは、薄ければ薄いほど電池の体積エネルギー密度や重量エネルギー密度が大きくなるので好ましいばかりでなく、強度そのものが相対的に低いので本発明の効果が特

に顕著となる。外装材の厚みは通常0.2 mm以下、好ましくは0.15 mm以下である。ただし、あまりに薄いのは強度不足が顕著になり、水分等も透過しやすくなるので、通常0.01 mm以上、好ましくは0.02 mm以上である。

【0036】外装材の材料としては、アルミニウム、ニッケルメッキした鉄、銅等の金属、合成樹脂等を用いることができる。好ましくは、ガスバリア層と樹脂層とが設けられたラミネートフィルム、特に、ガスバリア層の両面に樹脂層が設けられたラミネートフィルムである。このようなラミネートフィルムは、高いガスバリア性を有すると共に、高い形状可変性と、薄さを有する。その結果、外装材の薄膜化・軽量化が可能となり、電池全体としての容量を向上させることができる。

【0037】ラミネートフィルムに使用するガスバリア層の材料としては、アルミニウム、鉄、銅、ニッケル、チタン、モリブデン、金等の金属やステンレスやハステロイ等の合金、酸化ケイ素や酸化アルミニウム等の金属酸化物を使用することができる。好ましくは、軽重で加工性に優れたアルミニウムである。樹脂層に使用する樹脂としては、熱可塑性プラスチック、熱可塑性エラストマー類、熱硬化性樹脂、プラスチックアロイ等各種の合成樹脂を使うことができる。これらの樹脂にはフィラー等の充填材が混合されているものも含んでいる。

【0038】具体的なラミネートフィルムの構成としては、図13(A)に示すように、ガスバリア層40と樹脂層41が積層されたものを使用することができる。また、さらに好ましいラミネートフィルムは、図13(B)に示すようにガスバリア層40の外側面に外側保護層として機能するための合成樹脂層41を設けると共に、内側面に電解質による腐蝕やガスバリア層と電池要素との接触を防止したりガスバリア層を保護するための内側保護層として機能する合成樹脂層42を積層した三層構造体としたものである。

【0039】この場合、外側保護層に使用する樹脂は、好ましくはポリエチレン、ポリプロピレン、変性ポリオレフィン、アイオノマー、非晶性ポリオレフィン、ポリエチレンテレフタレート、ポリアミド等耐薬品性や機械的強度に優れた樹脂が望ましい。内側保護層としては、耐薬品性の合成樹脂が用いられ、例えばポリエチレン、ポリプロピレン、変性ポリオレフィン、アイオノマー、エチレン-酢酸ビニル共重合体等を用いることができる。

【0040】また、ラミネートフィルムは、図14に示すようにガスバリア層40と保護層形成用合成樹脂層41、耐蝕層形成用合成樹脂層42間にそれぞれ接着材層43を設けることもでき、また好ましい。さらにまた、外装材同士を接着するために、複合材の最内面に溶着可能なポリエチレン、ポリプロピレン等の樹脂からなる接着層を設けることもできる。これらの金属、合成樹脂あ

るいは複合材を用いてケースが形成される。ケースの成形はフィルム状体の周囲を融着して形成してもよく、シート状体を真空成形、圧空成形、プレス成形等によって絞り成形してもよい。また、合成樹脂を射出成形することによって成形することもできる。射出成形による場合は、ガスバリア層はスパッタリング等によって形成されるのが通常である。

【0041】外装材に凹部よりなる収容部を予め設けるには絞り加工等によって行うことができる。外装材は、加工が容易である点でフィルム状のものを使用するのが好ましい。正極、負極及び電解質を有する電池要素は、ケース内に収納される。前述のように、電池要素は、正極、負極及び電解質層からなる積層体（単位電池要素）を巻回して巻回形状とし、これをケース内に収納することもでき、また、上記積層体（単位電池要素）をそのまま平板形状でケース内に収納することもできる。さらに、前記図2、3に記載のように、単位電池要素を厚さ方向に複数個積層して電池要素とすることもできる。以下に単位電池要素の好適な構成について説明する。

【0042】図15は、このリチウム二次電池からなる単位電池要素の好適な一例を示すものである。この単位電池要素は、正極集電体22及び正極活物質層23からなる正極、スペーサ（電解質層）24、並びに、負極活物質層25及び負極集電体26からなる負極を積層したものである。リチウムデンドライトの析出を抑制するため、負極は正極よりも大きくされる。また、短絡を防止するため、スペーサ24は正極及び負極よりも大きくされる。スペーサを正負極よりも大きくすることによって、前述のように、単位電池要素のスペーサのはみ出し部相互を固着することができる。

【0043】この単位電池要素を複数個積層して電池要素とするのであるが、この積層に際しては、正極を上側とし負極を下側とした順姿勢（図15）の単位電池要素と、これとは逆に正極を下側とし負極を上側とした逆姿勢（図示略）の単位電池要素とを交互に積層する。即ち、積層方向に隣り合う単位電池要素は同極同士を（即ち、正極同士及び負極同士）が対面するように積層される。

【0044】この単位電池要素の正極集電体22からは正極タブ4aが延設され、負極集電体26からは負極タブ4bが延設されている。図15においては、正極集電体の片面、負極集電体の片面に、それぞれ正極活物質層、負極活物質層が形成されているように記載しているが、無論、集電体の両面に活物質層を形成することができる。この場合、同じ集電体の互いに反対の面に形成された活物質層は、相互に、異なる単位電池要素の構成要素とすることができる。

【0045】電極の平面形状は任意であり、四角形、円形、多角形等に行うことができる。図15の通り、集電体22、26には、通常、リード結合用のタブ4a、4

bが連設される。電極が四角形であるときは、通常図3に示すように電極の一边のサイド近傍に正極集電体より突出するタブ4aを形成し、また、負極集電体のタブ4bは他サイド近傍に形成する。

【0046】複数の単位電池要素を積層するのは、電池の高容量化を図る上で有効であるが、この際、単位電池要素それぞれからのタブ4aとタブ4bの夫々は、通常、厚さ方向に結合されて正極と負極の端子部が形成される。その結果、大容量の電池要素1を得ることが可能となる。タブ4a、4bには、図2に示すように、薄片状の金属からなるリード21が結合される。その結果、リード21と電池要素の正極及び負極とが電気的に結合される。タブ4a同士、4b同士の結合及びタブ4a、4bとリード21との結合はスポット溶接等の抵抗溶接、超音波溶着あるいはレーザ溶接によって行うことができる。

【0047】上記正極リードと負極リードの少なくとも一方のリード21好ましくは両方のリードとして、焼鈍金属を使用するのが好ましい。その結果、強度のみならず折れ曲げ耐久性に優れた電池とすることができる。リードに使用する金属の種類としては、一般的にアルミや銅、ニッケルやSUSなどを用いることができる。正極のリードとして好ましい材料はアルミニウムである。また、負極のリードとして好ましい材質は銅である。

【0048】リード21の厚さは、通常1 $\mu$ m以上、好ましくは10 $\mu$ m以上、更に好ましくは20 $\mu$ m以上、最も好ましくは40 $\mu$ m以上である。薄すぎると引張強度等リードの機械的強度が不十分になる傾向にある。また、リードの厚さは、通常1000 $\mu$ m以下、好ましくは500 $\mu$ m以下、さらに好ましくは100 $\mu$ m以下である。厚すぎると折れ曲げ耐久性が悪化する傾向にあり、また、ケースによる電池要素の封止が困難になる傾向にある。リードに後述する焼鈍金属を使用することによる利点は、リードの厚さが厚いほど顕著である。

【0049】リードの外部への露出長さは通常1mm以上50mm以下程度である。前記のように、電池要素は、正極及び負極を電解質層を介して積層した積層体（単位電池要素）を巻回してなる巻回型電池であってもよいが、この場合も、正極と負極との間にはスペーサを介在させ、これを正負極よりも大きくするのが好ましい。

【0050】以下、リチウム二次電池に使用する材料について説明する。電池要素は、通常正極と負極とそれらの間に存在する電解質層とを有する。正極及び負極は、通常、集電体とその上に設けられた活物質層を含む。正極集電体としては、アルミニウム、ニッケル、SUS等各種の金属を使用することができるが、好ましくはアルミニウムである。集電体の厚さは、通常1 $\mu$ m以上、好ましくは3 $\mu$ m以上、さらに好ましくは5 $\mu$ m以上であり、また、通常30 $\mu$ m以下、好ましくは25 $\mu$ m以

下、さらに好ましくは $20\mu\text{m}$ 以下である。薄ければ薄いほど、体積エネルギー密度及び重量エネルギー密度の観点から好ましいが、あまりに薄いのは強度等の点でハンドリングが困難になりやすい。集電体は、通常の金属箔のような板状や、パンチングメタルのようなメッシュ状であってよい。集電体の表面は、必要に応じて粗面化処理しておくことができる。

【0051】正極に用いることができる活物質としては、リチウムイオンを吸蔵放出可能な化合物として無機化合物でも有機化合物でも使用できる。無機化合物としてはFe、Co、Ni、Mn、等の遷移金属の酸化物、リチウムと遷移金属との複合酸化物、遷移金属硫化物等が挙げられる。具体的には、遷移金属酸化物として $\text{MnO}_2$ 、 $\text{V}_2\text{O}_5$ 、 $\text{V}_6\text{O}_{13}$ 、 $\text{TiO}_2$ 等を例示でき、リチウムと遷移金属との複合酸化物としてニッケル酸リチウム、コバルト酸リチウム、マンガン酸リチウム等を例示でき、遷移金属硫化物として $\text{TiS}_2$ 、 $\text{FeS}$ 等を例示できる。有機化合物としては、例えばポリアニリン等の導電性ポリマー等が挙げられる。また、これらの任意の無機化合物、有機化合物を任意の量混合して正極活物質として用いる方法も好適に使用される。好ましくは、リチウムと遷移金属との複合酸化物、特に、マンガン、ニッケル及びコバルトからなる群から選ばれる少なくとも1種の遷移金属酸化物とリチウムとを含有する複合酸化物である。中でも、コバルトとリチウムとを含む複合酸化物やニッケルとリチウムとを含む複合酸化物が好ましい。正極活物質の粒径は、レート特性、サイクル特性等の電池特性の点で、通常 $1\sim 30\mu\text{m}$ 、好ましくは $1\sim 10\mu\text{m}$ である。

【0052】負極集電体としては、銅、ニッケル、SU S等各種の金属を使用することができるが、好ましくは銅である。集電体の厚さは、通常 $1\mu\text{m}$ 以上、好ましくは $3\mu\text{m}$ 以上、さらに好ましくは $5\mu\text{m}$ 以上であり、また、通常 $30\mu\text{m}$ 以下、好ましくは $25\mu\text{m}$ 以下、さらに好ましくは $20\mu\text{m}$ 以下である。薄ければ薄いほど、体積エネルギー密度及び重量エネルギー密度の観点から好ましいが、あまりに薄いのは強度等の点でハンドリングが困難になりやすい。集電体は、通常の金属箔のような板状や、パンチングメタルのようなメッシュ状であってよい。集電体の表面は、必要に応じて粗面化処理しておくことができる。

【0053】負極に使用できる活物質としては、リチウム金属の外、リチウムを吸蔵放出可能な各種の化合物を使用することができる。具体的には、リチウム金属；リチウム-アルミニウム合金、リチウム-ビスマス-カドミウム合金、リチウム-スズ-カドミウム合金等のリチウム合金；グラファイト、コークス等の炭素材料等を挙げることができる。また、珪素、スズ、亜鉛、マンガン、鉄、ニッケル等の酸化物や硫酸鉛を使用することもできる。リチウム金属やリチウム合金を用いると、充電

の際にデンドライトが生成しやすく特に過充電時の安全性が低下する傾向にあるため、グラファイトやコークス等の炭素材料が好ましい。負極活物質の粒径は、初期効率、レート特性、サイクル特性等の電池特性の点で、通常 $1\sim 50\mu\text{m}$ 、好ましくは $15\sim 30\mu\text{m}$ である。

【0054】正極及び負極の活物質層は、通常上記活物質の外、バインダーを含有する。使用するバインダーとしては、電解液等に対して安定である必要があり、耐候性、耐薬品性、耐熱性、難燃性等が望まれる。バインダーとしてはシリケート、ガラスのような無機化合物や、主として高分子からなる各種の樹脂が使用できる。樹脂としては例えば、ポリエチレン、ポリプロピレン、ポリ-1,1-ジメチルエチレンなどのアルカン系ポリマー；ポリブタジエン、ポリイソブレンなどの不飽和系ポリマー；ポリスチレン、ポリメチルスチレン、ポリビニルピリジン、ポリ-N-ビニルピロリドンなどの環を有するポリマー；ポリメタクリル酸メチル、ポリメタクリル酸エチル、ポリメタクリル酸ブチル、ポリメタクリル酸メチル、ポリメタクリル酸エチル、ポリメタクリル酸、ポリメタクリル酸、ポリメタクリルアミドなどのアクリル誘導体系ポリマー；ポリフッ化ビニル、ポリフッ化ビニリデン、ポリテトラフルオロエチレン等のフッ素系樹脂；ポリアクリロニトリル、ポリビニリデンシアニドなどのCN基含有ポリマー；ポリ酢酸ビニル、ポリビニルアルコールなどのポリビニルアルコール系ポリマー；ポリ塩化ビニル、ポリ塩化ビニリデンなどのハロゲン含有ポリマー；ポリアニリンなどの導電性ポリマーなどが使用できる。また上記のポリマーなどの混合物、交成体、誘導体、ランダム共重合体、交互共重合体、グラフト共重合体、ブロック共重合体などであっても使用できる。これらの樹脂の分子量は、好ましくは $10000\sim 3000000$ 、さらに好ましくは $100000\sim 1000000$ である。低すぎると活物質層の強度が低下し、高すぎると粘度が高くなり電極の形成が困難になる傾向にある。

【0055】活物質100部に対するバインダーの配合量としては、好ましくは0.1-30部、さらに好ましくは1-20部である。バインダーの量が少なすぎると電極の強度が低下することがあり、多すぎるとイオン伝導度が低下する傾向にある。活物質層中には必要に応じて導電材料、補強材など各種の機能を発現する粉体、充填材などを含有していても良い。導電材料としては、上記活物質に適量混合して導電性を付与できるものであれば特に制限は無いが、通常、アセチレンブラック、カーボンブラック、黒鉛などの炭素粉末や、各種の金属のファイバー、箔などが挙げられる。炭素粉末導電性物質のDBP吸油量は $120\text{cc}/100\text{g}$ 以上が好ましく、特に $150\text{cc}/100\text{g}$ 以上が電解液を保持するという理由から好ましい。補強材としては各種の無機、有機の球状、繊維状フィラーなどが使用できる。

【0056】電極は、活物質層を構成する材料を含有する塗料を集電体上に塗布・乾燥することによって製造することができる。また、その後、活物質層を圧密処理に供することもできる。塗料の組成や、乾燥条件、圧密条件等を制御することによって、活物質層中におけるバインダーの体積分率は、制御することができる。必要に応じて、活物質層と集電体との間の接着性を向上させるため、これらの間にアンダーコートプライマー層を設けることができる。

【0057】アンダーコートプライマー層を用いる場合、その組成としてはカーボンブラック、グラファイト、金属粉体などの導電性粒子を添加した樹脂や、導電性の有機共役系樹脂を例示できる。好ましくは導電性粒子に、活物質としても機能しうるカーボンブラック、グラファイトを使用するとよい。また樹脂としても、活物質として機能しうるポリアニリン、ポリピロール、ポリアセチレン、ジスルフィド系化合物、ポリスルフィド系化合物などを用いると、容量を減少させないため好ましい。導電性粒子を添加した樹脂を主成分とする組成の場合、導電性粒子に対する樹脂の割合は、1-300重量%とすることが好ましい。低すぎると塗膜強度が低下して、電池使用時、工程上での剥離などが生じることがある。高すぎると伝導度が低下して電池特性が低下する傾向にある。特に好ましくは、5-100重量%の範囲とすることが好ましい。アンダーコートプライマー層の膜厚は、通常0.05-10 $\mu$ m、好ましくは0.1-1 $\mu$ mである。薄すぎると塗布が困難になり均一性が確保しにくくなる。厚すぎると電池の体積容量を必要以上に損なうことがある。

【0058】電解質は、正極と負極との間の電解質層の構成成分として存在する。また、電解質は、通常イオン移動相として電極の活物質中にも存在する。電解質としては、例えば電解液、高分子固体電解質、ゲル状電解質、無機固体電解質等各種の性状のものを用いることができる。一般に、高分子固体電解質、ゲル状電解質、無機固体電解質等の非流動性電解質を使用すれば、電解質のケース外部への漏れをより有効に防止することが可能となる。特に、本発明においては、ケースとして形状可変性を有するものを使用した場合、電解質がケース外部に漏れやすい傾向にあるので、非流動性電解質を使用する効果が特に顕著である。

【0059】一方、リチウム塩を非水系溶媒に溶解してなる電解液は、流動性が高く、一般に非流動性電解質に比べてイオン伝導性に優れる傾向にある。従って、電解液を含む電解質を使用するのは、イオン伝導性を向上させる点で好ましい。電解質として使用する電解液は、通常支持電解質であるリチウム塩を非水系溶媒に溶解してなる。非水系溶媒としては、比較的高誘電率の溶媒が好適に用いられる。具体的にはエチレンカーボネート、プロピレンカーボネート等の環状カーボネート類、ジメチ

ルカーボネート、ジエチルカーボネート、エチルメチルカーボネートなどの非環状カーボネート類、テトラヒドロフラン、2-メチルテトラヒドロフラン、ジメトキシエタン、ジフェニルエーテル等のエーテル類、 $\gamma$ -ブチラクトン等のラクトン類、スルフォラン等の硫黄化合物、アセトニトリル等のニトリル類等を挙げることができる。サイクル特性、レート特性、安全性等の電池特性上、好ましくは、環状カーボネート類及び/又はラクトン類である。

【0060】本発明においては、電解液の溶媒として、好ましくは常圧における沸点が150 $^{\circ}$ C以上の非水系溶媒（以下「高沸点溶媒」ということがある）を使用する。ここで、なお、「沸点がX $^{\circ}$ C以上」とは、圧力1 atmのもとで室温からX $^{\circ}$ Cまで加熱しても蒸気圧が1 atmを越えないことを意味する。即ち、圧力1 atmのもとで室温から150 $^{\circ}$ Cまで加熱した場合、常に蒸気圧が1 atm以下である非水系溶媒を使用するのが好ましい。その結果、より高いサイクル特性を得ることができる。例えば、ジメチルカーボネート、ジエチルカーボネート、ジメトキシエタン等の溶媒からなる低沸点溶媒を使用する場合、溶媒の気化により活物質と溶媒との間に気泡が発生して電解液の含浸状態の低下し、界面の不均一性が生じると共に、サイクル特性が低下しやすい傾向にある。また、高沸点溶媒を使用することによって、電池要素を形状可変性ケースに収納しても、高温下等での電池の形状変化（変形）、電解液の揮発、漏洩等を抑制することもできる。このような高沸点溶媒としては、プロピレンカーボネート、エチレンカーボネート、ブチレンカーボネート、 $\gamma$ -ブチラクトン等を挙げることができる。

【0061】なお、非水系溶媒は、粘度が1 mPa $\cdot$ s以上であることが好ましい。電解質に使用する支持電解質であるリチウム塩としては、LiPF<sub>6</sub>、LiAlF<sub>4</sub>、LiSbF<sub>6</sub>、LiBF<sub>4</sub>、LiClO<sub>4</sub>、LiI、LiBr、LiCl、LiAlCl<sub>2</sub>、LiHF<sub>2</sub>、LiSCN、LiSO<sub>3</sub>CF<sub>3</sub>等を挙げることができる。これらのうちでは特にLiPF<sub>6</sub>及びLiClO<sub>4</sub>が好適である。これら支持電解質の電解液における含有量は、通常0.5-2.5 mol/lである。

【0062】上記電解液とゲル形成用のポリマーとからゲル状電解質を構成することができる。ゲル状電解質は、通常、上記電解液をポリマーで保持してなる。ゲル状電解質は、電解液と同程度のイオン導電性を付与することできると共に、電解質を非流動化しているため、本発明においては、特に好ましい電解質である。ゲル状電解質におけるポリマーの電解液に対する濃度は、使用するポリマーの分子量にもよるが、通常0.1-30重量%である。濃度が低すぎるとゲルを形成しにくくなり、電解液の保持性が低下して流動、液漏れの問題が生じることがある。また濃度が高すぎると粘度が高くなりすぎ

て工程上困難を生じるとともに、電解液の割合が低下してイオン伝導度が低下しレート特性などの電池特性が低下する傾向にある。電解質を保持するポリマーとしては、ポリ(メタ)アクリレート系高分子や、アルキレンオキシドユニットを有するアルキレンオキシド系高分子、ポリフッ化ビニリデンやフッ化ビニリデン-ヘキサフルオロプロピレン共重合体のようなフッ素系高分子等、電解液をゲル化できる機能を有する各種のポリマーを挙げることができる。

【0063】ゲル状電解質を形成する方法としては、あらかじめポリマーを電解液に溶解させた電解質塗料を非流動化処理する方法や、電解液に重合性ゲル化剤を含有させた電解質塗料を架橋反応させて非流動性電解質とする方法など必要に応じた材料・製法を採用することができる。ゲル状電解質の形成を、電解液に重合性ゲル化剤を含有させた塗料を架橋反応させる方法で行う場合には、紫外線硬化や熱硬化などの重合処理を施すことによって高分子を形成するモノマーとなる成分を重合性ゲル化剤として電解液に添加することにより塗料を調製する。

【0064】重合性ゲル化剤としては、例えばアクリロイル基、メタクリロイル基、ビニル基、アリル基等の不飽和二重結合を有するものが挙げられる。具体的には、例えば、アクリル酸、アクリル酸メチル、アクリル酸エチル、エトキシエチルアクリレート、メトキシエチルアクリレート、エトキシエトキシエチルアクリレート、ポリエチレングリコールモノアクリレート、エトキシエチルメタクリレート、メトキシエチルメタクリレート、エトキシエトキシエチルメタクリレート、ポリエチレングリコールモノメタクリレート、N、N-ジエチルアミノエチルアクリレート、N、N-ジメチルアミノエチルアクリレート、グリシジルアクリレート、アリルアクリレート、アクリロニトリル、N-ビニルピロリドン、ジエチレングリコールジアクリレート、トリエチレングリコールジアクリレート、テトラエチレングリコールジアクリレート、ポリエチレングリコールジアクリレート、ジエチレングリコールジメタクリレート、トリエチレングリコールジメタクリレート、ポリエチレングリコールジメタクリレート、ポリアルキレングリコールジアクリレート、ポリアルキレングリコールジメタクリレート、トリメチロールプロパンアルコキシレートトリアクリレート、ペンタエリスリトールアルコキシレートトリアクリレート、ペンタエリスリトールアルコキシレートテトラアクリレート、ジトリメチロールプロパンアルコキシレートテトラアクリレートなどが例示できる。これらは複数種を併用することができる。これらの中で特に好ましくはエチレンオキシド基を複数含有するジアクリレート、トリアクリレートである。電解液中における重合性ゲル化剤の含有量は特に制限されないが、好ましくは1重量%以上

である。含有量が低いと高分子の形成効率が低下し、電解液を非流動化しにくくなる。他方、あまりに多すぎると未反応モノマーの残留や電解質塗料としての操作性が悪くなるので、通常30重量%以下とする。

【0065】ゲル状電解質を、あらかじめポリマーを含有した電解質塗料を非流動化する方法によって形成させる場合においては、ポリマーとして、高温で電解液に溶解し、常温でゲル状電解質を形成する高分子を使用するのが好ましい。即ち、高温で電解液に溶解したポリマーを常温にすることによってゲル状電解質とする。高温時の温度としては通常50~200℃、好ましくは100~160℃である。あまりにも低温で溶解するようであると、ゲル状電解質の安定性が低下する。溶解温度が高すぎると、電解液成分、ポリマー等の分解を引き起こすことがあり得る。非流動化の方法としては、電解液を室温で放置することが好ましいが、強制冷却することもできる。使用できるポリマーとしては、例えば、ポリビニルピリジン、ポリ-N-ビニルピロリドン等の環を有するポリマー；ポリメタクリル酸メチル、ポリメタクリル酸エチル、ポリメタクリル酸ブチル、ポリアクリル酸メチル、ポリアクリル酸エチル、ポリアクリル酸、ポリメタクリル酸、ポリアクリルアミドなどのアクリル誘導体系ポリマー；ポリフッ化ビニル、ポリフッ化ビニリデン等のフッ素系樹脂；ポリアクリロニトリル、ポリビニリデンシアニド等のCN基含有ポリマー；ポリ酢酸ビニル、ポリビニルアルコール等のポリビニルアルコール系ポリマー；ポリ塩化ビニル、ポリ塩化ビニリデン等のハロゲン含有ポリマー等が挙げられる。これらの中、好ましくはポリメタクリル酸メチル、ポリアクリロニトリル、ポリエチレンオキシド、あるいはそれらの変性体を使用する。上記のポリマーの混合物、変成体、誘導体、ランダム共重合体、交互共重合体、グラフト共重合体、ブロック共重合体等を使用することもできる。

【0066】これらのポリマーの重量平均分子量は、好ましくは10,000~5,000,000の範囲である。分子量が低いとゲルを形成しにくくなり、他方、あまり分子量が高いと粘度が高くなりすぎて取り扱いが難しくなる。これらのゲル状電解質を形成する方法の中では、電解液に重合性ゲル化剤を含有させた電解質塗料を架橋反応させて非流動性電解質とする方法が、電極間の密着性が向上し、本発明の効果が特に顕著となるため好ましい。

【0067】電解質中には、必要に応じて、電池の性能向上のために各種の添加剤を添加することができる。このような機能を発現させる添加剤としては、特に限定はされないが、トリフルオロプロピレンカーボネート、1,6-ジオキサスピロ[4,4]ノナン-2,7-ジオン、1,2-クラウン-4-エーテル、ビニレンカーボネート、カテコールカーボネート、無水コハク酸などが挙げられる。



【0068】電解質層は、通常、多孔性シートからなるスペーサ中に電解質を含浸させてなる。スペーサは、正極と負極との間に設けられた多孔性の膜であり、これらを隔離すると共に、電解質層を支持する。スペーサの材料としては、ポリエチレンやポリプロピレン等のポリオレフィン類や、これらの水素原子の一部又は全部がフッ素原子で置換されたポリオレフィン類、ポリアクリロニトリル、ポリアラミド等の高分子を挙げることができる。好ましくは、ポリオレフィンやフッ素置換されたポリオレフィン類である。具体的には、ポリエチレン、ポリプロピレン、ポリテトラフルオロエチレン、ポリフッ化ビニリデン等を挙げることができる。無論、上記ポリマーのモノマーユニットを含む共重合体や、ポリマーの混合物であってもよい。スペーサは、1軸延伸や2軸延伸によって形成された延伸フィルムであってもよく、また、不織布であってもよい。スペーサの膜厚は、通常100 $\mu$ m以下、好ましくは50 $\mu$ m以下、さらに好ましくは30 $\mu$ m以下、最も好ましくは20 $\mu$ m以下である。膜厚が大きすぎると電池のレート特性や体積エネルギー密度が低下する傾向にある。また、薄すぎると、剛性不足によって切断が困難になる傾向にあり、また短絡が生じやすいので、通常5 $\mu$ m以上、好ましくは7 $\mu$ m以上、さらに好ましくは8 $\mu$ m以上である。スペーサの空隙率は、通常45-90%、好ましくは45-75%である。空隙率が大きすぎると機械的強度が不足し、小さすぎると電池のレート特性等が低下する傾向にある。

#### 【0069】

【実施例】以下、本発明を実施例に基づいてさらに詳細に説明するが、本発明は下記実施例により何ら限定されるものではなく、その要旨を変更しない範囲において適宜変更し実施することができる。なお以下の説明において「部」とあるのは、特に断らない限り重量部を示す。

#### 正極製造例1

コバルト酸リチウム90部、アセチレンブラック5部、ポリフッ化ビニリデン5部及びN-メチル-2-ピロリドン80部を混練機により2時間混練し正極塗料1とした。

【0070】次に、正極塗料1を20 $\mu$ m厚のアルミニウム集電体基材上に、エクストルージョン型のダイコーティングによって塗布、乾燥し、活物質がバインダーによって集電体上に結着された多孔質膜からなる活物質層を形成させた。ついで、ロールプレス（カレンダー）を用いて圧密後、切断し、正極1とした。

#### 負極製造例

グラファイト（粒径15 $\mu$ m）90部、ポリフッ化ビニリデン10部及びN-メチル-2-ピロリドン100部を、混練機により2時間混練し負極塗料1とした。

【0071】次に、負極塗料1を20 $\mu$ m厚の銅集電体基材上にエクストルージョン型のダイコーティングによ

って塗布、乾燥し、活物質がバインダーによって集電体上に結着された多孔質膜からなる活物質層を形成させた。ついで、ロールプレス（カレンダー）を用いて圧密後、切断し、負極1とした。

#### 電解質塗料作成例1

1M濃度のLiPF<sub>6</sub>を含有する、エチレンカーボネート、プロピレンカーボネート及びフェニルエーテルの混合液（体積比率；エチレンカーボネート：プロピレンカーボネート：フェニルエーテル=7：3：7：3：1）92.5部、テトラエチレングルコールジアクリレート44部、ポリエチレンオキシドトリアクリレート22部、重合開始剤2部及び添加剤（無水コハク酸）9部を混合攪拌溶解し、電解質塗料1とした。

#### 実施例1

正極1、負極1に電解質塗料1を塗布し、別に電解質塗料1に浸したポリエチレン製多孔質フィルムを間に挟んで積層した後、90℃で10分加熱することにより電解質を非流動化して、図9に示すような、正極、負極、及び非流動化性電解質を有する平板状の単位電池要素を作成した。

【0072】得られた単位電池要素を積層後、正極同士ならびに負極同士の端子部を束ね、それぞれの端子部に電流を取り出すリードを接続した。その後、アルミニウム層の両面に樹脂層を有する厚さ約100 $\mu$ mのラミネートフィルムを対向成形した図9のような外装材に収容した。その後、ラミネートフィルムを真空シールで封入後、リードを取り出した辺を除く接合片部（図5において、接合片部4Aに相当）を被包部に沿うように折曲した。このように作成した平板状電池Aの電池容量は650mAhであった。

【0073】上記のように作成した平板状電池Aを、0.65Aの定電流で、公称使用電圧間の放電を3サイクル行った。この電池を、電池の全厚さの110%に空隙高さをネジで調整した図22のような組立型金属製収容部材に挟み、過充電試験を行った。即ち、上限電圧を10Vに設定し、電池を放電状態から1.8C（1.17A）の定電流で200分間充電し続けた。放電状態の電池の厚みは3.9mm（電極の厚みは3.7mm）であった。過充電時のガスの漏洩は全く観測されず、電池表面の最高温度は94℃であった。また過充電後の電池にはガスによる電池の膨れは殆ど観測されず、僅かに電池が緩む程度であった。なお、過充電後の電池の厚みは4.2mm（電極の厚みは4.0mm）であった。このような電池は、過充電後に電池に圧力を加えても外装材の破れによるガスの漏洩は観測されなかった。

【0074】また、上記と同様の方法で平板状電池Aを収容部材に挟み、上限電圧を10Vに設定し、電池を放電状態から1.95Aの定電流で120分間充電し続けた結果、過充電時のガスの漏洩は全く観測されず、電池表面の最高温度は132℃であった。また過充電後の電



池にはガスによる電池の膨れは殆ど観測されず、僅かに電池が緩む程度であった。尚、過充電後の電池の厚みは4.3mm(電極の厚みは3.8mm)であった。このような電池は、過充電後に電池に圧力を加えても外装材の破れによるガスの漏洩は観測されなかった。

#### 参考例

上記のように作成した平板状電池A(平板面積15cm<sup>2</sup>)を、0.85Aの定電流で、公称使用電圧間の充放電を3サイクル行った。放電状態の電池の厚みは3.9mm(電極の厚みは3.7mm)であった。次に上限電圧を10Vに設定し、電池の膨れに応じ荷重をかける方法で電池を放電状態から1.8C(1.17A)の定電流で200分間充電し続けた。その結果、過充電後の電池にはガスによる電池の膨れは全く観測されず、過充電後の電池の厚みは4.6mm(電極の厚みは4.3mm)であった。この際、電池にかけた最大荷重は8.3kg(8.3/15=0.55kg/cm<sup>2</sup>)であった。なお、この際の電池表面の最高温度は8.5℃であった。

#### 比較例1

収容部材に平板状電池Aを収容しなかったこと以外実施例1と同様にして、電池Aの過充電試験を行なった。

【0075】その結果、過充電中に電池は膨れ、72分後に発煙し、過充電時のガスの漏洩が観測された。その際の電池表面の最高温度は140℃であった。同様の条件で上限電圧を10Vに設定し、電池を放電状態から1.95Aの定電流で充電し続けた結果、38分後に電池は発火した。参考例から、過充電時に電池に特定(0.5kg/cm<sup>2</sup>以上)の圧力を加えることによって過充電時の電池の安全性を向上できることが分かる。即ち、過充電時にこの荷重に相当する力が加わるように収容部材を設計すれば、過充電時の安全性が向上することが分かる。実際、実施例1と比較例1とを比較すると、過充電時に圧力が加わるように収容部材に電池を収納することによって過充電時の安全性は向上している。

#### 【0076】

【発明の効果】本発明によれば、過充電時の安全性にかかわる固有の問題を解明し、過充電時の電池の膨れを抑制することにより、過充電時の使用機器の損傷ならびに発生ガスによる使用機器の腐食や有機ガス等の有毒ガスの漏洩を防止すると共に電池の安全性を向上させた二次電池を提供することができる。従って、本質安全機能を有する二次電池が実現し、仮に他の過充電対策を施さなくても相対的により安全な二次電池とすることができる。また、他の過充電対策と併用することによってより安全なリチウム二次電池とすることができる。

#### 【図面の簡単な説明】

【図1】実施の形態に係る電池の分解斜視図である。

【図2】実施の形態に係る電池の要部の断面図である。

【図3】実施の形態に係る電池の電池要素を示す斜視図

である。

【図4】実施の形態に係る電池の斜視図(接合片部の固着前)である。

【図5】実施の形態に係る電池の斜視図(接合片部の固着後)である。

【図6】実施の形態に係るケースの断面図である。

【図7】電池が膨れる様子を示す模式的断面図である。

【図8】別の実施の形態に係るケースの断面図である。

【図9】別の実施の形態に係る電池の製造途中の斜視図である。

【図10】さらに別の実施の形態に係る電池の製造途中の斜視図である。

【図11】さらに異なる実施の形態に係る電池の製造途中の斜視図である。

【図12】図11の製造途中の平面図である。

【図13】(A)、(B)図はそれぞれ外装材を構成する複合材の一例を示す縦断面図である。

【図14】外装材を構成する複合材の他の例を示す縦断面図である。

20 【図15】単位電池要素の一例の模式的な断面図である。

【図16】電池要素のタブ部分の拡大断面図である。

【図17】別の実施形態に係る電池の斜視図である。

【図18】本発明の一実施形態に係る収容部材の模式的な分解斜視図である。

【図19】電池要素が収容部材に収納された様子を示す、図18のA-A矢視断面図である。

【図20】本発明の別の実施形態に係る収容部材の模式的な分解斜視図である。

30 【図21】本発明のさらに別の実施形態に係る収容部材の模式的な分解斜視図である。

【図22】本発明のさらに別の実施形態に係る収容部材の模式的な分解斜視図である。

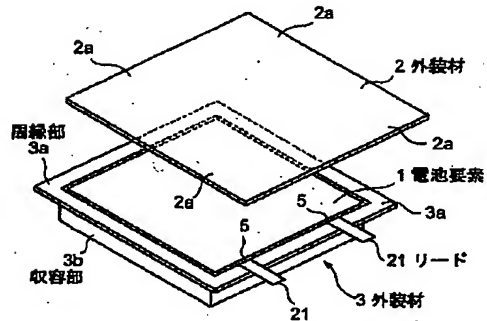
#### 【符号の説明】

- 1 電池要素
- 2、3、6、7、8 外装材
- 4a、4b タブ
- 4A、4F、4G 接合片部
- 4B 被包部
- 5 絶縁材料
- 11 正極
- 11a 正極活物質
- 12 負極
- 12b 負極活物質
- 13 非流動性電解質層
- 15a 正極集電体
- 15b 負極集電体
- 21 リード
- 22 正極集電体
- 23 正極活物質

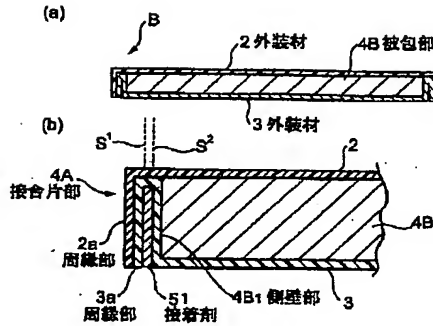
23  
24 スペース (電解質層)  
25 負極活物質  
26 負極集電体  
40 金属層

24  
\* 41、42 合成樹脂層  
43 接着剤層  
181 収容部材  
\*

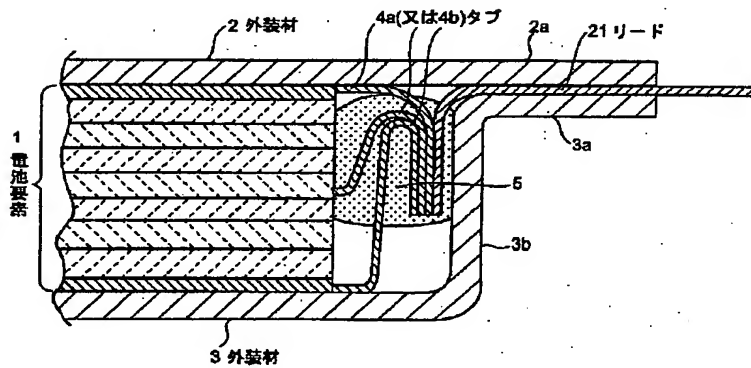
【図1】



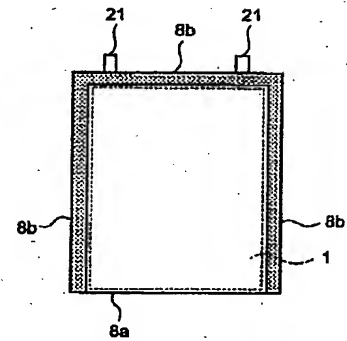
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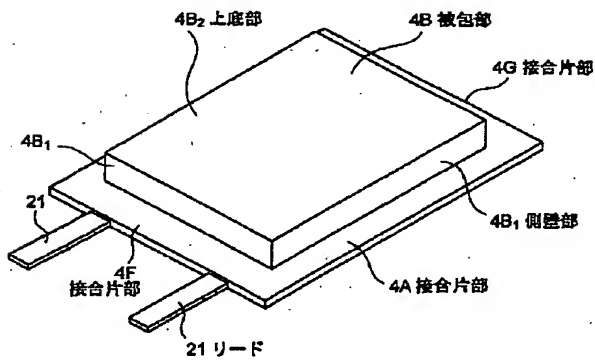
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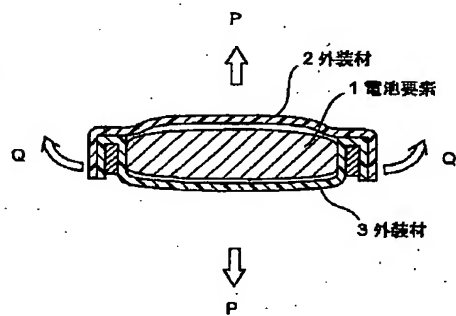
【図12】



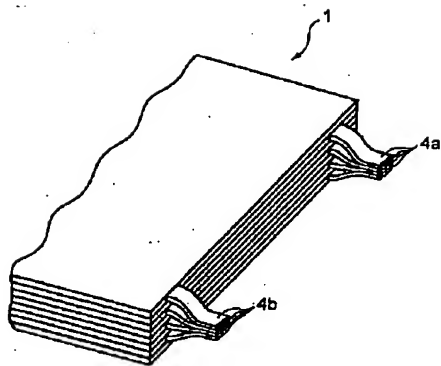
【図4】



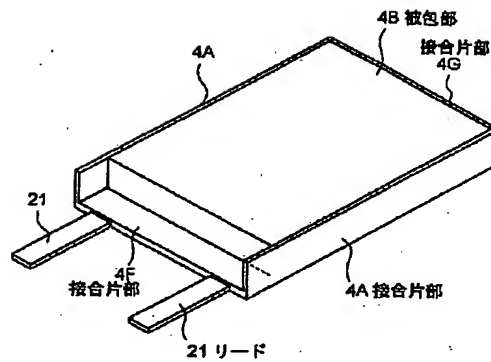
【図7】



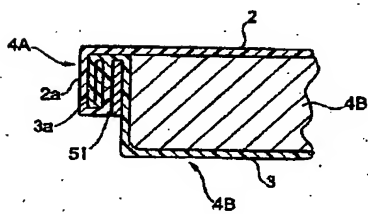
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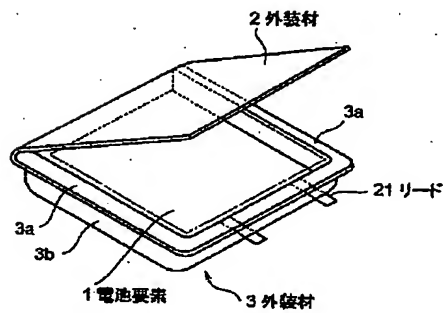
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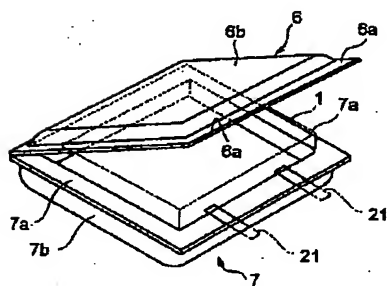
【図8】



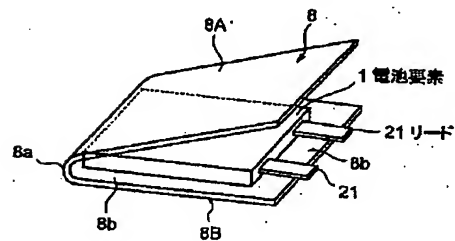
【図9】



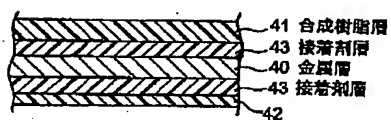
【図10】



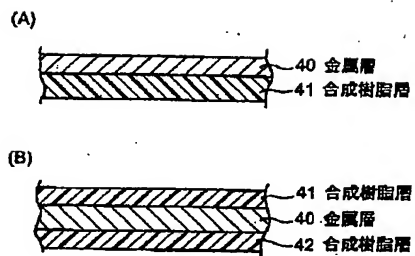
【図11】



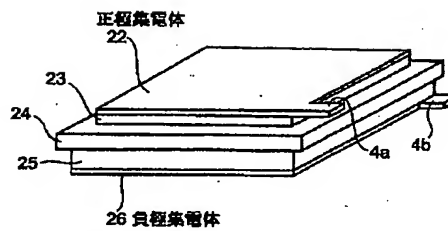
【図14】



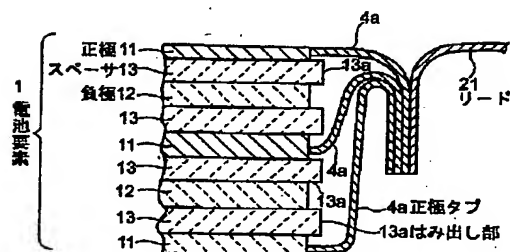
【図13】



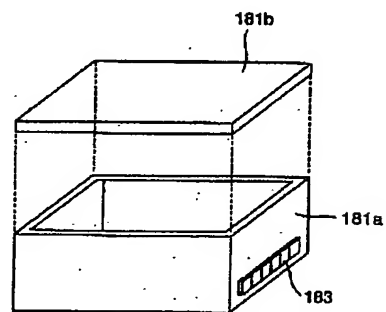
【図15】



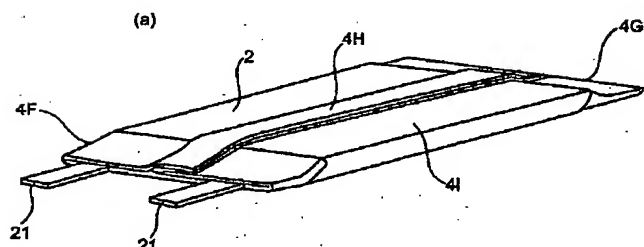
【図16】



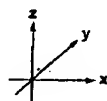
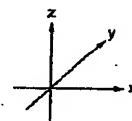
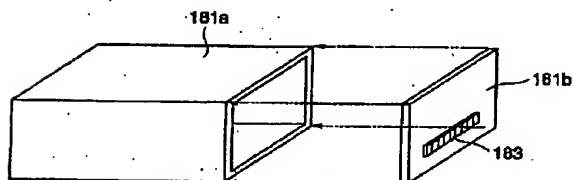
【図21】



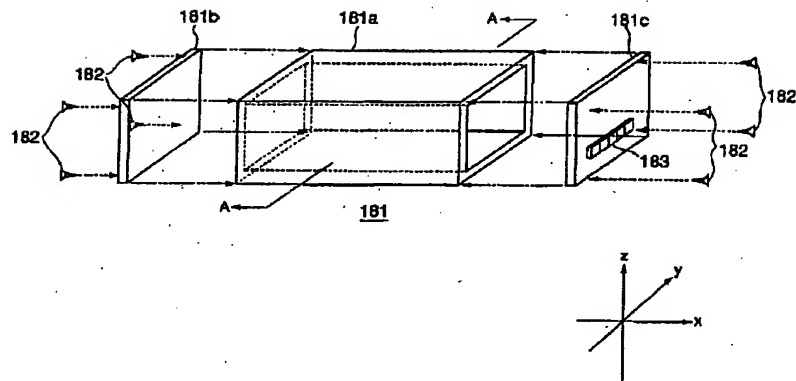
【図17】



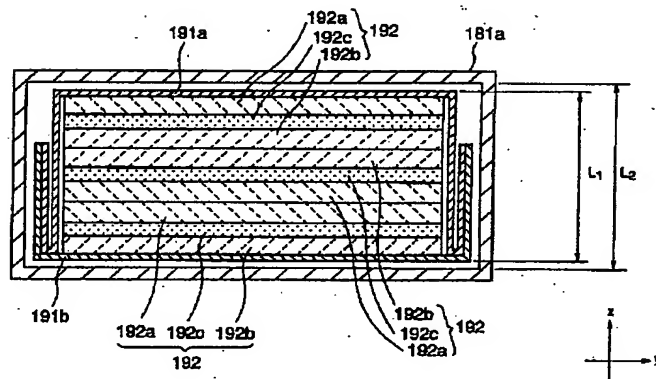
【図20】



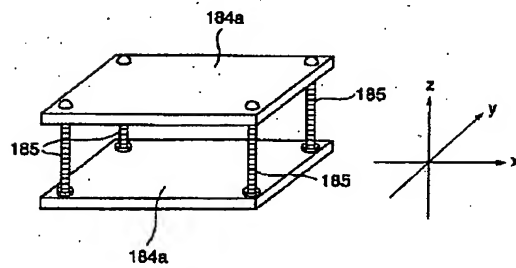
【図18】



【図19】



【図22】



## フロントページの続き

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EJ05 EJ12 HJ04 HJ15 HJ19  
5H040 AA14 AA31 AA34 AS11 AS12  
AS13 AS14 AS15 AS17 AS18  
AS19 AS22 AS23 AS24 AS25  
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AY08 CC05 CC20 LL01 LL06  
LL10 NN01 NN05